Analytical Abstracts

A monthly publication dealing with all branches of analytical chemistry: issued by the Society for Analytical Chemistry

Volume 6
No. 9, Abstracts 3367–3852

September, 1959

Published for the Society by
W. HEFFER & SONS LTD., CAMBRIDGE, ENGLAND

Binding . . .

W. Heffer & Sons Ltd. announce that they are now able to BIND copies of ANALYTICAL ABSTRACTS, in an approved binding case, at a cost of 12/6 per volume. The 12 Parts for 1958 together with Index and remittance for 12/6 should be sent to

W. HEFFER & SONS, LIMITED
HILLS ROAD, CAMBRIDGE

IMPORTANT NOTICE TO SUBSCRIBERS

(Other than Members of the Society)

The Subscription to *Analytical Abstracts*, inclusive of Index, is £5 per annum; and for *Analytical Abstracts* together with *The Analyst* and Indexes is £8 8s. per annum.

The price of single copies of *Analytical Abstracts*, including back numbers, is 10s. 6d. post free.

Analytical Abstracts is available printed on one side of the paper only, suitable for incorporation into reference systems; the cost is £5 7s. 6d. per annum, exclusive of Index.

All further enquiries about subscriptions should be made through the Secretary, the Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1. Telephone: BELgravia 3258.

ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

3367. **Seventh Colloquium Spectroscopicum Internationale. September, 1958.** Organised by the Association des Ingénieurs sortis de l'Université de Liège. *Rev. Univ. Min.*, 1959, **15** (5).—The following papers of analytical interest are published (in French unless otherwise stated). **Infra-red spectroscopy and its applications to industry,** H. W. Thompson, 225–230. **The present state and future prospects in emission spectroscopy,** W. F. Meggers, 230–237 (in English). **New methods in spectroscopic techniques (possibilities of interference spectroscopy),** P. Jacquinot, 237–249. **Evolution of emission spectral techniques in industrial control in Belgium,** V. Mathieu and A. Hans, 250–256. **Infra-red spectra between 1·1 and 2·5 microns,** G. Hepner, 256–258. **Analysis of bands of a new system attributed to the molecule N_2^+,** J. Janin and J. d'Incan, 258–261. **Ratio of the intensity of the components of the doublets in the spectra of aluminium, indium and thallium,** D. Kunisz, 263. **The spectrometric determination under controlled atmospheres of carbon in metals,** R. Breckpot, J. Morris and K. de Clippeleir, 266–270 (in English). **Experiences with vacuum-spectrometric analysis of carbon, sulphur and phosphorus in steel,** S. Eckhard, G. Graue and R. Marotz, 270–275 (in German). **The emission characteristic of the C III 2296·86 line of the different spark zones and their application to carbon determination in steel,** T. Török and G. Szikora, 275–278 (in German). **Emission-spectrometric determination of the gaseous elements in metals,** V. A. Fassel, W. A. Gordon, R. J. Jasinski and F. Monte Evens, 278–281 (in English). **Recent results obtained with the Quantovac in the analysis of steel,** W. H. Barry and J. M. Carrol, 281–289. **Automatic spectrometric determination of phosphorus and the usual accompanying elements of steel in one exposure and with one excitation,** G. Graue, S. Eckhard and R. Marotz, 290–296 (in German). **Industrial analysis of titanium and zirconium and their alloys,** J. Orsag, 296–299. **Determination of lead in aviation spirit,** J. M. Lopez de Azcona, 299. **Spectrographic analysis of pure copper by the globule arc procedure,** G. Maassen, 300–303 (in German). **Ternary alloys of lead. Spectrographic analysis and the effect of the thermal history,** E. Asensi Álvarez-Arenas and A. Sampedro Piñeiro, 303–306. **The accuracy of a semi-quantitative analytical procedure,** E. Golling, 306–309 (in German). **A spectrographic method for the rapid determination of germanium,** P. S. Tutundžić and V. Šćepanović, 309–313. **The influence of metallic state on the spectral emission of carbon steels,** A. Camuñas, 313–315. **Contribution to the problem of the third constituent in quantitative emission spectrography,** O. Werner, 315–319 (in German). **The glow discharge in the spectrochemical analysis of solutions. I,** Z. Šternberg, 337–339; **II,** Z. Šternberg and M. Kajzer, 339–341 (in English). **Spectral analysis by a shaking method,** J. Czakow, 341–343 (in German). **The use of a discharge tube for gas analysis,** C. Smit and J. A. Smit, 350–353 (in English). **Some new data on the method of emission-spectrochemical analysis in the far ultra-violet,** J. Romand, G. Balloffet and B. Vodar, 353–356. **Spectrographic method with controlled energy of emission for the analysis of mineral substances,** P. Herman and Z. Hainski, 378–383. **Indirect flame-photometric determination of beryllium in beryllium bronze,** J. Malinowski and D. Dancewicz, 405–407 (in German). **The effect of ethylene-diaminetetra-acetic acid on the emission of strontium in the oxy-acetylene flame in the presence of certain disturbing elements,** J. Debras and I. A. Voinovitch, 408–411. **New trends in infra-red spectroscopy,** G. B. B. M. Sutherland, 412–417 (in English). **The calibration of infra-red spectrometers of medium and low dispersion,** R. N. Jones, P. K. Faure and W. Zaharias, 417–422 (in English). **New techniques for micro and trace analysis in fundamental and far infra-red,** H. J. Heidiger, 427–430 (in English). **Determination of mixtures of water and deuterium oxide by infra-red. Determination of molecular extinction coefficients,** M. Ceccaldi, 430–436. **Non-dispersive infra-red analysis of mixtures of water and heavy water,** C. A. Bosselaar, 436–439 (in English). **Recent advances in Raman spectroscopy,** A. C. Menzies, 470–479 (in English). **X-ray spectroscopy,** L. S. Birks, 526–530 (in English). **The analysis of small quantities of material by X-ray fluorescence,** N. W. H. Addink, 530–532 (in English). **New technique of X-ray spectrometry,** R. Griffoul and R. Rabillon, 533–535. **Applications of X-ray spectrometry,** R. Rabillon and R. Griffoul, 536–538. **The Castaing electronic probe micro-analyzer and its applications,** J. Philibert and J. Descamps, 539–543. **Rapid analysis of copper, zinc and cobalt by X-ray fluorescence in mineral powders and concentrates,** A. Hans, 544–548. **X-ray fluorescence analysis of powders,** F. J. Haftka, 549–555 (in German). **Quantitative analysis by X-ray fluorescence: detection of niobium in complex minerals,** M. Mariee, 555–558. **Nuclear and electronic magnetic resonance,** B. Bleaney, 559–563 (in English). **Spectral determination of carbon and sulphur in industrial control,** V. Mathieu and M. Lacomble, 597–598.

3368. **X-ray fluorescence spectroscopy in chemical analysis.** E. T. Hall. *Endeavour*, 1959, **28**, 83–87.—A review.

3369. **A mixture of aqua regia and potassium iodide as oxidation agent and solvent.** D. Prístavka (Dept. Anal. Chem., High-School of Chem. Technol., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1958, **12** (11), 682–683.—A mixture of KI, HNO_3 and

HCl has been found useful for dissolving various materials, *e.g.*, alloys, special steels, pyrites. *Procedure*—Mix the sample with an equal amount of KI and add aqua regia dropwise (violent reaction); then add 2 to 3 ml of aqua regia in excess and heat. Dissolution is complete within 20 min. Sodium iodide must be used in place of KI when dissolving platinum alloys, to prevent the formation of slightly sol. potassium salts. When dissolving pyrites or sulphur-containing organic compounds, the sample is treated with KI and 5 to 6 ml of HNO_3 and, after 2 min., 3 ml of conc. HCl is added. No separation of elementary sulphur has been observed.

J. ZÝKA

3370. **The analytical use of diarylboric acids [diarylborinic acids] and especially of tetraphenyl diboroxide.** R. Neu (Arzneimittelfabrik Dr. W. Schwabe, G.m.b.H., Karlsruhe-Durlach, Germany). *Chemist Analyst*, 1958, **47** (4), 106–109.—The properties of the diarylborinic acids are discussed, and directions are given for the preparation of tetraphenyl diboroxide and 2-aminoethyl- and 2-amino-2-methyl-1-propyl-diphenylborate, and for their use in the detection of hydroxyphenylbenzo-δ-pyrones, of choline and -onium compounds, and of surface-active compounds, and for the determination of 8-hydroxyquinoline and of flavones.

R. E. ESSERY

3371. **Steric hindrance in analytical chemistry. V. A new 2-substituted 8-hydroxyquinoline (oxine).** H. Irving and D. J. Clifton (Inorg. Chem. Lab., Oxford Univ.). *J. Chem. Soc.*, 1959, 288–290.—2-(1-Ethylpropyl)-8-hydroxyquinoline (**I**) is prepared (method described) and the sensitivity of its reaction towards Cu^{2+}, Zn^{2+}, Al^{3+} and In^{3+} is compared with that of 2-methyl- (**II**), 2-phenyl- (**III**), 5-methyl- and unsubstituted 8-hydroxyquinoline. The sensitivity is determined in buffers at pH 5·14, 8·4 and 12·4. The sensitivity of **I** for Cu^{2+} and Zn^{2+} is comparable with that of **II** and **III**, and like all 2-substituted oxines it gives no ppt. with Al^{3+}. With In^{3+}, **I** gives a ppt. even at pH 12·4 and this is accounted for by the "weighting effect" and the higher basicity which more than compensates for the steric effect.

E. J. H. BIRCH

3372. **4-(2-Pyridylazo)resorcinol as a possible analytical reagent for the colorimetric determination of cobalt, lead and uranium.** F. H. Pollard, P. Hanson and W. J. Geary (Dept. of Phys. and Inorg. Chem., Univ. of Bristol, England). *Anal. Chim. Acta*, 1959, **20** (1), 26–31.—This reagent (preparation described) gives colours with many heavy-metal ions, but not with ions of the alkaline-earth and alkali metals. It is claimed to be valuable for the colorimetric determination of Co, Pb and U, since it has high sensitivity and is soluble in water.

W. T. CARTER

3373. **Application of thio salts in analysis. IV. A new scheme of qualitative analysis. Part C.** G. B. S. Salaria (Chem. Dept., Gov. Coll., Rohtak, Punjab, India). *Anal. Chim. Acta*, 1958, **19** (6), 605–606.—Observations on an earlier scheme (*Anal. Abstr.*, 1956, **3**, 1599) include suggestions for improving efficiency and new procedures for the detection of metals of the copper group and the iron - aluminium group in the presence of phosphate.

T. R. ANDREW

3374. **Thermal stability of analytical standards. VI.** C. Duval (Lab. de Recherches Micro-Anal., École Nat. Supérieure de Chim., Paris). *Anal. Chim. Acta*, 1959, **20** (1), 20–25 (in French).—The thermolysis curves and i.r. absorption spectra of the following substances have been determined—$NaNO_3$, $SrS_2O_3.H_2O$, $Na_2H_3IO_6$, $AlCl_3.6H_2O$, $K_2S_2O_8$, $Na_2S_2O_7$, $FeSO_4.7H_2O$, nitrilotriacetic acid, molybdophosphoric acid, aluminium ammonium sulphate, ammonium ferrous sulphate and ammonium ferric sulphate.

W. T. CARTER

3375. **New pH indicator.** M. Z. Barakat, S. K. Shehab and M. M. El-Sadr (Biochem. Dept., Fac. of Vet. Med., Giza, Cairo). *Analyst*, 1958, **83**, 695–696.—A new pH indicator is prepared by condensing Na 1:2-naphthaquinone-4-sulphonate with 2:4-dinitrophenylhydrazine. The colour change is from rose-red at pH values below 8·4 to violet at values above 9·2. The indicator has been used in determining the acidity of urine and vinegar, the acid value of oils and water-insol. organic acids and also in the urease test. It is not suitable for titrating free H_2SO_4 in a soln. of $CuSO_4$ or for assaying vegetable alkaloids. It forms crimson crystals with strychnine, a purple - violet colour with brucine and an intense blue colour with atropine. It can be used for the differentiation of strychnine and brucine.

A. O. JONES

3376. **Omega Chrome black PPV [C.I. Mordant Black 39], a new metal indicator.** A. A. Abd El Raheem and Abdel-Aziz Amin (Min. of Public Health Lab., Cairo, Egypt). *Z. anal. Chem.*, 1959, **165** (6), 416–421 (in English).—The use of Omega Chrome black PPV is described for the EDTA titration of Zn, Mn, Ni, Cd, Mg and Pb. The limits of detection of the end-points were determined and the accuracy of titration was ±1%. The indicator was suitable for the titration of mixtures of Mn and Zn, the error being ≯1%. The colour reactions of 20 metals with the indicator are listed.

G. P. COOK

3377. **Preparation of stable standard sulphatocerate solutions.** S. Carrano and A. F. McGuinn (Dept. of Chem., Fairfield Univ., Conn., U.S.A.). *Chemist Analyst*, 1958, **47** (4), 103–104.—For the preparation of stable sulphatocerate soln., the heat of dilution of the H_2SO_4 should be fully utilised, and dilution carried out slowly. To 200 ml of conc. H_2SO_4 add 700 g of ceric ammonium sulphate, mix to a slurry and allow to stand for 24 hr., with occasional stirring. Then make successive additions of 250-ml portions of water, with manual stirring, allowing the temperature to develop fully between each addition, as shown by a thermometer. When the vol. has reached 3 litres, complete the dissolution, if necessary, by heating at 60° till the soln. is perfectly clear. Cool to room temp., and add water slowly, with vigorous swirling, till the vol. reaches 10 litres. Soln. so prepared (0·1 *N* in 1·0 *N* H_2SO_4) have remained clear, stable, and constant in titre for at least 12 months.

R. E. ESSERY

3378. **Manganimetry. I. Preparation, standardisation and stability of manganic pyrophosphate solution.** Masayoshi Ishibashi, Tsunenobu Shigematsu and Shozo Shibata (Chem. Dept., Kyoto Univ., Sakyo-ku, Tokyo). *Japan Analyst*, 1958, **7** (10), 644–646.—Standard $MnHP_2O_7$ soln. is prepared by treating $MnCl_2$ (12·5 g) in 3 *M* $K_4P_2O_7$ (100 ml) with $KMnO_4$ (1 g). The MnO_2 is filtered off, the

filtrate brought to pH 4·5 with *N* NaOH, the MnO_2 is filtered off, and the filtrate is made acid with H_2SO_4 (1 : 1) to remove K_2SO_4, and stored at pH 4 to 6. The oxidation of Mn^{2+} is also effected with conc. HNO_3 (10 ml) by heating to dryness and washing the residue with acetone and ether. The product dissolved in water gives the same absorption curve as that prepared by Belcher and West's method (*Anal. Chim. Acta*, 1950, **6**, 322). For the standardisation, $(NH_4)_2SO_4.FeSO_4.6H_2O$ is the best reagent.

II. Direct oxidimetric titration of quinol with manganic pyrophosphate. Masayoshi Ishibashi, Tsunenobu Shigematsu and Shozo Shibata. *Ibid.*, 1958, **7** (10), 647–649.—Quinol (3 to 10 mg) is titrated with $MnHP_2O_7$ soln. (0·03 to 0·07 *N*) in 2 to 4 *N* H_2SO_4, either potentiometrically at −0·5 V *vs.* the S.C.E. or with diphenylamine soln. (0·2%, 0·2 ml) as indicator. In >7 *N* H_2SO_4 or >5 *N* HCl, *p*-benzoquinone interferes. K. SAITO

3379. **The EDTA titration: applications. V. Conclusion.** H. Flaschka, A. J. Barnard, jun., and W. C. Broad (Dept. of Chem., Georgia Inst. of Technol., Atlanta, U.S.A.). *Chemist Analyst*, 1958, **47** (4), 109–112.—A literature survey is presented, which covers the determination of pharmaceutical and organic compounds, the analysis of biological materials, the determination of the hardness of water, recent developments in the use of dyes and other organic compounds as indicators for the EDTA titration, and the radiometric detection of the end-point. (97 references.) R. E. ESSERY

3380. **EDTA titrations without metal indicators.** Buddhadev Sen (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (6), 551–554.—Metal ions whose EDTA complexes have formation constants >15 may be titrated by adding an excess of EDTA (disodium salt) and back-titrating with standard Co^{2+} soln. The test soln. (≃25 ml) should be at pH 7; 1 ml of saturated NH_4SCN soln. and an equal vol. of acetone are added. The appearance of the blue cobalt thiocyanate colour marks the end-point. Good results are reported for Th^{4+}, Pb^{2+}, Ni^{2+} and VO^{2+}; Hg^{2+} and Cu^{2+} cannot be titrated by this method. T. R. ANDREW

3381. **Complexometric titrations (chelatometry). XL. Back-titration, with pyrogallol red or bromopyrogallol red as indicator.** M. Malát, V. Suk and M. Tenorová (Inst. Anal. Chem., Charles' Univ., Prague). *Chem. Listy*, 1958, **52** (12), 2405–2407.—*Back-titration with* $Bi(NO_3)_3$—Dilute the soln. of Pd^{2+}, Tl^{3+}, Fe^{3+}, In^{3+}, Ga^{3+} or Bi^{3+} (in the form of nitrates) to 100 ml and add an excess of EDTA (disodium salt) (**I**) (0·05 to 0·01 *M*). Adjust the pH to 2 to 3, add pyrogallol red soln. (**II**) or bromopyrogallol red soln. (**III**) (0·05% in 50% ethanol) (15 drops) as indicator and titrate the yellow soln. with 0·1 *M* $Bi(NO_3)_3$ till red or violet - red; add the 0·1 *M* $Bi(NO_3)_3$ in slight excess and titrate back with **I** till yellow, to increase the accuracy in the determination of the end-point; 1 to 10 mg of Pd, 2 to 35 mg of Tl, 0·6 to 100 mg of Fe, 0·1 to 170 mg of In, 0·3 to 85 mg of Ga and 2 to 100 mg of Bi can be determined; Zn, Mn, Cd, Ag, Be, Ge, rare- and alkaline-earth metals and NH_4^+ do not interfere. In the presence of Ni, Al, Cu and Hg, the titration must be carried out at a higher temp. An excess of Hg^{2+} can be removed by the addition of ascorbic acid. Coloured ions (Co, Cu, Ni, Cr and U) interfere when present in excess; Pd can be determined in the presence of Pt, Rh and Ir. *Back-titration with* $Pb(NO_3)_2$—Dilute the sample of Pd^{2+}, Ni^{2+}, Ga^{3+}, In^{3+}, Bi^{3+}, Tl^{3+}, Fe^{3+}, V^{4+}, Cu^{2+}, Th^{4+}, Co^{2+} or Pb^{2+} to 100 ml, add an excess of **I**, together with indicator, adjust the pH to 5, add Na acetate soln. (20%) (5 to 6 ml) and titrate with 0·05 to 0·01 *M* $Pb(NO_3)_2$ till violet (**II**) or blue - violet (**III**); add a slight excess of the $Pb(NO_3)_2$ soln. and titrate with **I** till red; 0·5 to 10 mg of V, 1 to 10 mg of Pd, 1·5 to 35 mg of Tl, 0·5 to 30 mg of Fe, 0·6 to 16 mg of Cu, 1 to 23 mg of In, 3 to 13 mg of Ga, 2 to 180 mg of Th, 0·6 to 30 mg of Ni, 0·5 to 30 mg of Co, 2 to 100 mg of Bi and 2 to 200 mg of Pb can be determined. The presence of Ca, Ba, Mg and Sr causes no interference if **II** is used as indicator; Li, K, Ag, Cr, NH_4^+, Cl^-, ClO_4^-, NO_3^- and SO_4^{2-} do not interfere even when present in 500 to 1000-fold excess. The average error in both procedures is ±0·2%. The method has been applied to the analysis of an alloy of Ag and In (9 : 1). J. ZÝKA

3382. **Tetraethylenepentamine, a selective titrant for metal ions. Potentiometric end-point detection.** C. N. Reilley and A. Vavoulis (Dept. of Chem., Univ. of N. Carolina, Chapel Hill, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 243–248.—Methods are given for the titration of Hg, Cu, Ni, Zn and Cd, singly and in various mixtures, with tetraethylenepentamine (**I**) and a mercury electrode for potentiometric end-point detection. The alkaline-earth and rare-earth metals, Al, Bi, Pb and Sc do not interfere. The reaction of **I** with the elements quoted is discussed theoretically in relation to the effect of pH, complex formation and hydrolysis. It is shown that potential *vs.* pH diagrams obtained when a mercury electrode is used give a means of predicting optimum titration conditions and of detecting the relative effect of competing equilibria. On theoretical and practical grounds it is shown that **I** is superior to triethylenetetramine as a selective titrant for metal ions. F. L. SELFE

See also Abstract—**3523**, Removal of H_2SO_4 from H_3PO_4.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

3383. **Direct titration of hydrochloric - sulphuric acid and nitric - sulphuric acid mixtures in acetone. Automatic derivative potentiometric or spectrophotometric end-point detection.** H. V. Malmstadt and D. A. Vassallo (Univ., Urbana, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 206–210.—In the procedures given, the proton from HCl or HNO_3 and the first proton from H_2SO_4 are titrated together to the first end-point. The second proton from H_2SO_4 is then titrated to the final end-point. The titration is made with tri-*n*-butylmethylammonium hydroxide (0·1 *N* soln. in dry benzene) on a 5- or 10-ml aliquot of the sample soln. in the presence of acetone (90%). Both end-points are sharp and can be determined successively, to within 0·01 ml, either potentiometrically with platinum (10% Rh) - graphite electrodes or spectrophotometrically at 575 mμ, using in each instance the automatic derivative method. For high accuracy a correction should be made for the amount of acetic acid in the

acetone and of CO_3^{2-} in the titrant. For concn. of H_2SO_4, HCl and HNO_3 of $\simeq 0{\cdot}5$ milli-equiv. each, the error is $\simeq \pm 0{\cdot}3\%$ for each acid.

W. J. BAKER

3384. **Ion-exchange separation of metal ions.** J. S. Fritz and G. R. Umbreit (Inst. for Atomic Res., Iowa State Coll., Ames, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (6), 509–516.—Separation of metal ions can be effected by cation-exchange resins in the presence of EDTA at a pH such that one ion is firmly complexed and another almost completely dissociated. Retention on a Dowex 50-X4 resin column is recorded against pH for Bi^{3+}, Fe^{3+}, Zr^{4+}, Cu^{2+}, Sc^{3+}, Th^{4+}, Yb^{3+}, Hg^{2+}, Zn^{2+}, Y^{3+}, Sm^{3+} and La^{3+}. The effect of changing the column length and ion concn. is reported. Conditions are given for the separation of equimolecular mixtures of La and Th, Sm and Fe, Y and Sc, and Mg and Al.

T. R. ANDREW

3385. **Ion-exchange separation of metals by a single-pass method.** R. T. Oliver and J. S. Fritz (Ames Lab., Ames, Iowa). *U.S. Atomic Energy Comm.*, Rep. ISC-1056, 1958, 4 pp.—A single-pass method for the ion-exchange separations of binary mixtures of metals is described, and experimental applications are presented. The method consists in complexing each of the components in the mixture with a separate complexing agent at a pH sufficient to ensure max. co-ordination of the metals. The complexing agents are chosen so that the metal complexes formed are of opposite charge. The mixture is then passed through an ion-exchange resin which adsorbs one species completely, allowing the other to be collected in the eluate. An anion- or cation-exchange resin is used. Sulphosalicylic acid was used to form a negative complex with Fe, U, Al, Th, Zr or Y. Ethylenediamine was used to form a positive complex with Cu, Zn, Ni or Cd. Quant. separations of binary mixtures containing one metal from each of these groups were performed at pH values 8, 9 and 10 with Dowex (nuclear sulphonic cation-exchange resin) and Amberlite IRA-401 (quaternary amine anion-exchange resin).

NUCL. SCI. ABSTR.

3386. **Determination of copper, lead, tin and antimony by controlled-potential electrolysis. III. Adaptation of the method to the analysis of some alloys.** B. Alfonsi (Res. and Control Lab. Auto-Avio, FIAT, Turin, Italy). *Anal. Chim. Acta*, 1958, **19** (6), 569–575.—Previous work (*cf. Anal. Abstr.*, 1959, **6**, 2468) has been extended to cover the analysis of tin-base bearing alloys, leaded bronze, Ag - Cu - Cd - Zn alloys and Cu - Cd alloys.

T. R. ANDREW

3387. **Potentiometric titration of silver, copper, lead and thallium with thioacetamide.** L. M. Andreasov, E. I. Vall, V. A. Kremer and V. A. Shelikhovskiĭ (A. M. Gorky Kharkov State Univ.). *Zhur. Anal. Khim.*, 1958, **13** (6), 657–660.—The pptn. of metals by thioacetamide can be speeded up by an addition of a small amount of hydrazine hydrate, and this enables Cu, Pb and Tl to be determined potentiometrically. Such an addition is not necessary in the potentiometric determination of Ag^+ as sulphide, the pptn. being rapid enough in ammoniacal medium. For the determination of Cu, to a 10-ml aliquot of the sample soln. in dil. HNO_3 (containing 0·01 to 0·015 g of Cu^{II}) add 30 ml of *N* Na acetate and 5 ml of aq. NH_3 (25%), followed by hydrazine hydrate soln. (1:5), dropwise, until the blue colour is discharged. Then titrate with thioacetamide. An excess of hydrazine hydrate in the soln. should be avoided. Similar determinations are described for Ag, Pb, Tl and mixtures of Ag and Cu.

W. ROUBO

3388. **Indirect mercurimetric determination of cadmium, cobalt, nickel and zinc by means of their pyridine - thiocyanate complexes.** J. Bognár and S. Sárosi (II Chem. Dept., Tech. Univ. for Heavy Ind., Miskolc, Hungary). *Magyar Kém. Foly.*, 1959, **65** (1), 28–30.—Details are given of a method in which the metals are pptd. as complexes with pyridine and NH_4SCN, with a composition varying from $M(Py)_2(SCN)_2$ to $M(Py)_4(SCN)_2$. The ppt. is dissolved in *N* H_2SO_4 and the SCN^- are titrated with 0·1 *N* $Hg(NO_3)_2$ in the presence of $K_3Fe(CN)_6$ and Xylenol blue VS (*cf.* Bognár and Jellinek, *Anal. Abstr.*, 1958, **5**, 2623; Bognár, *Ibid.*, 1958, **5**, 3661). A determination takes 15 to 25 min.

A. G. PETO

3389. **Application of alginic acid as an ion exchanger. I. The separation and determination of various metal ions [iron, aluminium and copper].** Takeo Takahashi and Satoru Emura (Inst. Ind. Sci., Tokyo Univ., Yayoicho, Chiba). *Japan Analyst*, 1958, **7** (9), 568–571.—The separation of Fe^{III}, Al and Cu with alginic acid as ion exchanger (Specker and Hartkamp, *Z. anal. Chem.*, 1953, **140**, 167; Specker *et al.*, *Ibid.*, 1954, **141**, 33) was examined by the batch method. The time taken for reaching the equilibrium state is $\simeq 5$ hr. for Fe and $\simeq 8$ hr. for Al. Dil. H_2SO_4 is used as eluting agent, and Fe^{3+}, Cu^{2+} and Al^{3+}, eluted in this order, are determined complexometrically. The K_d value for Fe is almost independent of the amount of Al but it decreases when the concn. of Fe is $>0{\cdot}001$ *M*. Specker's results for the separation were confirmed.

K. SAITO

3390. **Rapid determination of iron, aluminium, calcium and magnesium in the presence of manganese by the use of CyDTA [1:2-diaminocyclohexanetetra-acetic acid] and EDTA. Application to the analysis of basic open-hearth furnace slag.** Yoshihide Endo (Fukiai Plant, Kawasaki Steel Corp., Wakihama, Fukiai-ku, Kobe). *Japan Analyst*, 1958, **7** (10), 611–616.—The EDTA titration of Fe^{3+} at pH 1·5 to 2·2 with salicylic acid (**I**) as indicator and of Al at pH 2 to 2·2 with Cu - 1-(2-pyridylazo)-2-naphthol (**II**) (*cf.* Flaschka and Abdine, *Anal. Abstr.*, 1957, **4**, 361) can be applied in the presence of Mn, Ca and Mg by using 1:2-diamino*cyclo*hexanetetra-acetic acid (**III**). Provided that Mn^{2+} are masked with EDTA, **III** does not interfere with the pptn. of Ca oxalate at pH 3·5 to 4·2. The sum of Ca and Mg is titrated with EDTA in the presence of tri-ethanolamine and KCN. The time taken for a determination is $\simeq 50$ min. *Procedure*—Dissolve the sample in HCl (15 ml) and H_2O_2 (30%, a few drops), dilute to 150 ml and add ammonium acetate soln. (25%, 10 ml) and HCl (1:1) or aq. NH_3 soln. (1:1) to give a pH of 1·5. Heat the soln. to 30°, add **I** (0·1 g) and titrate with 0·05 *M* **III** (for Fe). Add $Cu(NO_3)_2$ soln. (0·05 *M*, 1 ml), adjust the pH to 2 to 2·2 with ammonium acetate soln. (5%), boil, add **II** soln. (0·1%, 2 to 3 drops) and titrate the hot soln. with 0·05 *M* **III** (for Al). Dilute the soln. to 250 ml, add EDTA (0·1 *M*, 5 to 10 ml) to a 100-ml portion and aq. NH_3 soln. to make the pH 3·5 to 4·4 and boil with ammonium oxalate soln. (5%, 20 ml) to precipitate Ca. Make another 100-ml portion ammoniacal (pH 10) with NH_4Cl soln.

(20%, 20 ml), triethanolamine (5 ml) and KCN (20%, 15 ml) and titrate with 0·05 *M* EDTA, with Eriochrome black T as indicator (for the sum of Ca and Mg). K. SAITO

3391. Group separation of fission products with an anion-exchange resin in the oxalate form. Seishi Yajima, Eiji Shikata and Chizuko Yamaguchi (Japan Atomic Energy Res. Inst., Tokai, Ibaragiken). *Japan Analyst*, 1958, **7** (11), 721.—When mixed fission products (aged for 3 years) in 0·5% NH_4Cl soln. (pH 6, 20 ml) are passed through a column (diam. 6 mm, length 10 cm) of Dowex 1-X7·5 (50 to 100 mesh), ^{137}Cs and ^{90}Sr pass through without being adsorbed. Rare-earth elements (^{90}Y, ^{144}Ce, ^{147}Pm), ^{95}Zr, ^{95}Nb and ^{106}Ru are eluted in this order from the resin phase with 0·2 *N*, 0·5 *N*, 1 *N* HCl and 2 *N* HNO_3, respectively. K. SAITO

3392. Titrimetric analysis of white metals. L. J. Ottendorfer (Inst. of Inorg. and Anal. Chem., Univ. of Technol., Vienna, Austria). *Chemist Analyst*, 1958, **47** (4), 96–101.—Dissolve the sample (0·5 g) in conc. HCl (10 ml) and conc. HNO_3 (2 ml), avoiding unnecessary heating. Add 25 ml of 4% aq. KCl soln. and 25 ml of 0·2 *M* EDTA (disodium salt), boil gently for 1 min., cool, and dilute to 250 ml. *Procedure for total Sn and Pb*—Transfer an aliquot (25 ml) to a 250-ml conical flask, add satd. aq. thiourea soln. till the blue colour due to copper is discharged, add 0·5 ml in excess, then add 15 ml of 30% aq. hexamine soln., dilute to 150 ml, and back-titrate the excess of EDTA with 0·05 *M* $Pb(NO_3)_2$ to a red end-point with xylenol orange. *Procedure for Sn*—To the soln. from the first titration add 2 g of NaF. Tin is thus freed from its EDTA complex, and the EDTA so liberated is titrated with 0·05 *M* $Pb(NO_3)_2$, the end-point being a red colour which is stable for 1 min. *Procedure for total Sn, Pb and Cu*—To a second aliquot (25 ml) add 15 ml of 30% aq. hexamine soln., dilute to 150 ml, and back-titrate the excess of EDTA with standard Pb soln. as described above. *Procedure for Sb*—Dissolve a fresh sample of the metal (0·5 g) in 10 to 15 ml of conc. H_2SO_4 with heating, continue heating to fuming and fume for 2 min. in the open beaker to remove SO_3. Cool, add successively 20 ml of water, 20 ml of conc. HCl and 100 ml of hot water, and titrate the Sb with 0·1 *N* $KBrO_3$ at 70°, with methyl orange as indicator, the end-point, which should be approached slowly, being the discharge of the pink colour. The suspended $PbSO_4$ does not interfere. Results for three alloys of known composition show satisfactory recoveries. R. E. ESSERY

3393. Determination of water by titration with coulometrically generated Karl Fischer reagent. A. S. Meyer, jun., and C. M. Boyd (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 215–219.—Microgram amounts of H_2O in organic solvents, *e.g.*, glycols and strong amines, can be determined by titration with Karl Fischer reagent produced by the electrolytic generation of iodine in a soln. of the depleted reagent in ethanediol. The end-point is reached when an excess of iodine is generated, and is detected by the depolarisation of platinum indicator-electrodes. Assuming 100% current efficiency, 1 mole of iodine is equiv. to 1 mole of H_2O or 10·71 coulombs of generating current per mg of H_2O. Side reactions that consume iodine are eliminated by a supplementary generating current, adjusted to maintain the soln. at the end-point before the addition of the sample (1 ml). The more basic amines, *e.g.*, 1:2-diaminopropane, should be neutralised with a 15% w/v soln. of salicylic acid in ethanediol (instead of acetic acid in methanol) to reduce the rate of esterification. The procedure is applicable to concn. of H_2O as low as 5 to 50 μg per ml, although the accuracy is higher for samples containing 500 to 1000 μg per ml (coeff. of variation $<2\%$). The sensitivity is $\simeq 2$ μg per ml. Limitations of the method are discussed; an advantage is the time saved by eliminating the preparation, standardisation, storage and measurement of the Karl Fischer reagent. W. J. BAKER

3394. Determination of traces of nickel in sodium metal. T. M. Florence (Australian Atomic Energy Comm., Res. Estab., Sutherland, N.S.W.). *Anal. Chim. Acta*, 1958, **19** (6), 548–551.—The nickel-cyanide complex absorbs strongly at 268 mμ; Co^{2+}, Mo^{6+}, Cr^{3+} and Cu^{2+} interfere. The sample is dissolved in abs. ethanol, acidified with a 5-ml excess of conc. HCl, evaporated to dryness and dried for 2 hr. at 120°. Dissolve the residue in the minimum of 0·1 *N* HCl and dilute to a known vol. Dilute an aliquot (5 to 75 μg of Ni) to 10 ml then add 1 drop of HNO_3 and boil; add 0·5 g of NH_4Cl and 0·5 g of urea, boil till the pH has risen to 6 to 7, then simmer for 15 min. and filter. Wash the ppt. with 1% NH_4Cl soln., add 5 drops of hydroxylamine hydrochloride soln. (10%) to the filtrate and boil. Cool, add 2·5 ml of KCN soln. (5%) and dilute to 25 ml. Read at 268 mμ against 0·5% KCN containing hydroxylamine hydrochloride. T. R. ANDREW

3395. Use of sulphuric acid to depress the interference of calcium in the determination of sodium with an EEL flame photometer. R. D. Bond and J. T. Hutton (C.S.I.R.O., Div. of Soils, Adelaide, S. Australia). *Analyst*, 1958, **83**, 684–686.—In the relatively low-temp. coal gas - air flame of the EEL flame photometer all Ca salts are not volatilised to the same extent. Addition of phosphate has a depressive effect on the emission of Ca, but the effect is not constant and depends on the presence of other anions. Sulphate also depresses the Ca emission of $CaCl_2$ to a lower extent than PO_4^{3-}, but the depression is independent of other ions and is determined solely by the concn. of Ca. Quoted results of the effect of the addition of different amounts of H_2SO_4 to $CaCl_2$ soln. in the flame photometer with the "calcium" interference filter in position show that the Ca emission is progressively decreased until the H_2SO_4 added is equiv. to the Ca present. In the determination of Na in soln. containing Ca by means of the EEL flame photometer, H_2SO_4 should be added in an amount at least equiv. to the Ca present, and if the soln. contains anions such as PO_4^{3-} or HCO_3^- an additional amount of H_2SO_4 equiv. to any other metal ions present should be added. With a suitable filter, Ca emission can be determined and a correction can be applied to the Na value if, as often happens, the amount of Ca present is known. A. O. JONES

3396. Rapid flame-photometric micro-determination of sodium, potassium and lithium in glass. A. J. Hegedüs and M. Dvorszky (Forschungsinst. f. d. nachrichtentech. Ind., Tungsram, Budapest). *Mikrochim. Acta*, 1959, (1), 160–161.—The finely ground sample (20 to 50 mg) is evaporated to dryness with 1 ml of HF, dissolved in 10 drops of HNO_3 and re-evaporated to dryness. The residue is

dissolved in 2 ml of HNO_3 (10%) and diluted to 50 to 250 ml according to the expected content of alkali metal. Jena interference filters (SIF 589a, SIF 768a and SIF 670a) are used in the flame-photometric determination. T. R. ANDREW

3397. **Use of a flame photometer for the determination of sodium and potassium oxides in the routine control of glass compositions.** E. Walton and T. Robinson (Osram Glass Wks, Lemington, England). *J. Soc. Glass Tech.*, 1958, **42**, 271T–278T.—The sample (25 mg, 120 mesh) is decomposed with HF (1 ml) plus $HClO_4$ (10 drops); the mixture is evaporated to dryness and the residue is dissolved in warm HCl (1:4) (5 ml). The soln. is made up to 250 ml and an aliquot is taken for the determination of Na and K in an EEL flame photometer. After deducting the reagent blank, the percentages of Na_2O and K_2O are read from calibration curves, prepared from readings on soln. of a similar glass (made synthetically) covering a range of contents of Na_2O and K_2O. Between different laboratories the results are reproducible to within 2% of the amount of oxide being determined. The method has been found to be particularly suitable for the furnace control of an "alkali-free" glass which actually contains $\simeq$0·25% of Na_2O and 0·10% of K_2O.
W. J. BAKER

3398. **Determination of micron-sized particles. Detection of potassium ion.** B. J. Tufts (Cloud Physics Lab., Dept. of Meteorol., Univ. of Chicago, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 242–243.—Airborne particles containing K may be detected and their size and number determined after reaction with sodium tetraphenylboron (1% aq. soln.). The air sample is drawn through a membrane filter, which is then floated on a few ml of the reagent soln. in a Petri dish, and washed by floating twice for 5 min. on water. After drying, the filter is mounted on a glass slide with immersion oil. The reaction sites are observed, as white granular spots, by microscopic examination under dark-ground illumination. The reaction sites may be counted and there is a definite ratio of particle size to size of reaction site. A ppt. with the reagent is formed by NH_4^+. This ion does not interfere under ordinary circumstances, as the ppt. forms only after exposure for 30 min. to the reagent soln. F. L. SELFE

3399. **Rapid analysis of gamma-emitters using gamma-ray scintillation spectrometer. II. Determination of caesium-137 in fission products.** Fumio Aoki, Seishi Yajima and Toshio Kurosawa (Gov. Chem. Ind. Res. Inst., Shibuya-ku, Tokyo). *Bull. Chem. Soc. Japan*, 1959, **32** (1), 42–45 (in English).—A simple and reliable analysis is achieved by combining the use of anion-exchange resins (Dowex 1-X7·5) in the oxalate and carbonate forms with measurement by a γ-ray scintillation spectrometer. Several similar aliquots are taken from the fission-products soln., to which are added various known amounts of pure ^{137}Cs. The bulk of the uranium is extracted with tributyl phosphate - diethyl ether (1:1). The samples are then percolated through a mixed bed of the carbonate and oxalate forms of the resin. The alkali metals pass through. Each percolate is measured by using a γ-ray scintillation spectrometer, and the real peak height of the 0·66 MeV gamma is plotted against the amounts of added ^{137}Cs soln. The straight line is then determined by the method of least squares, and the amount of ^{137}Cs in the fission product is given by the length of the abscissa between its intersection with the straight line and the origin.
I. JONES

3400. **Potentiometric titration at constant current of copper(II) in ammoniacal medium.** E. R. Nightingale, jun. (Sch. of Chem., Univ. of Minnesota, Minneapolis, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (6), 587–592.—Cupric ions can be determined with EDTA (disodium salt) in air-free ammoniacal medium by using the technique of potentiometric titration at constant current (5 μA) with a rotating platinum electrode - S.C.E. pair. Attempts to titrate with benzoin α-oxime gave poor results unless the ppt. was removed by centrifuging or filtration after each addition of reagent.
T. R. ANDREW

3401. **Determination of oxygen in copper.** W. F. Harris and W. M. Hickam (Res. Lab., Westinghouse Electric Corp., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 281–283.—The sample (2 to 3 g) in a graphite boat is heated under high vacuum to 1150°. Under these conditions, essentially the only gas present is CO and the gas pressure can be measured with a mercury manometer. The CO pressure is related to oxygen content by calibration. The method is simple and rapid in operation, the time required for a determination being 15 min. The standard deviation for a single determination is $\pm$28 μg of O, so that the method is suitable for refinery control. The method is not subject to errors due to the presence of S in the copper. The theoretical basis for the non-interference of S is discussed. The apparatus used is described and illustrated. F. L. SELFE

3402. **Metallurgical polarographic analysis. VII. Simultaneous determination of cadmium, nickel and zinc in copper-base alloys.** Yoshiaki Miura (Yawata Iron and Steel Works, Fukuoka-ken). *Japan Analyst*, 1958, **7** (12), 783–785.—When Cu is pptd. as CuSCN, Cd, Ni and Zn remaining in the filtrate can be simultaneously determined in a supporting electrolyte containing NH_4Cl and aq. NH_3 soln., in the presence of Na_2SO_3 and gelatin. There is no interference from SCN^-, ClO_4^- or Na. The wave of Co overlaps that of Zn and a large amount of Mn interferes with the determination of Zn. *Procedure*—Dissolve the sample (0·2 g) in aqua regia (5 ml) and heat with $HClO_4$ (60%, 5 ml) to white fumes. Cool, neutralise with 5 *N* NaOH, add $HClO_4$ (5 *N*, 2 ml), saturated Na_2SO_3 soln. (1 ml), *M* KSCN (10 ml) and water (50 ml) and boil for 1 min. Cool, filter, wash the ppt. with 0·1% KSCN soln. containing 0·01% of Na_2SO_3 and make up the filtrate and washings to 100 ml. Dilute an aliquot to 50 ml with 2 *M* NH_4Cl containing 2 *N* aq. NH_3 (25 ml), saturated Na_2SO_3 soln. (2·5 ml) and gelatin soln. (1%, 0·5 ml) and record the polarogram.
K. SAITO

3403. **Determination of a trace of bismuth in pure silver. I. Co-precipitation with aluminium hydroxide.** Michihiro Ishibashi, Toyoshi Nagai, Taitiro Fujinaga and Wataru Funasaka (Fac. of Engng, Kyoto Univ., Sakyo-ku, Kyoto). *Japan Analyst*, 1958, **7** (9), 553–556.—Aluminium hydroxide (2·7 mg of Al) can be used in place of Fe for the co-pptn. of Bi (0·00005 to 0·002%) and the Bi is polarographically determined in *N* HNO_3 containing 0·01 *M* Na_2SO_3 and 0·01% gelatin. The recovery of Bi decreases with increasing concn. of NH_3, pH 8·2

being the optimum for the pptn. of Al. The working curve is linear for <220 μg of Bi per 25 ml of the supporting electrolyte. The sample soln. is heated for 30 min. on a water bath with $Al(NO_3)_3$ soln. (0·1 *M*, 1 ml), NH_4NO_3 soln. (4 *M*, 5 ml) and aq. NH_3 soln. (1·5 *M*) and then for 10 min. with a further addition of aq. NH_3 soln. (10 ml). The ppt. is filtered off, dissolved in 5 *N* HNO_3, re-pptd., dissolved in 5 *N* HNO_3, evaporated to dryness and dissolved in the supporting electrolyte (25 ml) for polarography. K. SAITO

3404. **Spectrophotometric determination of traces of gold with Rhodamine B.** Hiroshi Inoshi (Gov. Ind. Res. Inst., Nagoya, Japan). *Mikrochim. Acta*, 1959, (1), 9–17 (in English).—To 1 to 10 μg of Au in 80 ml of 3 *N* HCl add 1·0 ml of $TeCl_4$ soln. (1 mg of Te per ml) and heat to boiling. Add successively 15 ml of satd. SO_2 soln., 10 ml of hydrazine hydrochloride soln. (15%) and a further 20 ml of satd. SO_2 soln. Boil gently until the ppt. has coagulated (5 to 15 min.) and set aside for 1 hr. Filter off the ppt. on a sintered glass filter (porosity 4) and wash it five times with 2 *N* HCl. Add 1 ml of aqua regia to the pptn. beaker, heat almost to boiling and pour through the filter. Repeat with a further 1 ml and finally wash four times with water. Evaporate the aqua regia soln. and washings to dryness, moisten with 1 drop of aqua regia and set aside for 1 to 2 min. Add 2·5 ml of HCl (6 *N*) and transfer to a separating-funnel with 1·0 ml of water. Wash out the beaker into the funnel with 5·0 ml of NH_4Cl soln. (30%) and 10·5 ml of water. Mix, add 1·0 ml of Rhodamine B (C.I. Basic Violet 10) soln. (0·2%), mix, add 10·0 ml of benzene and shake for 1 min., then transfer the benzene layer to a centrifuge tube. Centrifuge for 5 min. at 2000 r.p.m. and record the extinction of the soln. against benzene in a 1-cm cell at 565 mμ within 30 min. A calibration curve is prepared by carrying out the colour formation as described above (from the addition of 2·5 ml of 6 *N* HCl onwards) on pure Au soln. Beer's law is obeyed up to 10 μg. The extinction of 10 μg of Au at 565 mμ is $\simeq$0·6 in a 1-cm cell. Antimony, Ga, Fe, Pt and Tl do not interfere; 1 mg of Sn gives a colour equivalent to 0·7 μg of Au. T. R. ANDREW

3405. **Separations involving sulphides. VIII. Separation of ruthenium and indium from alkaline-earth metals.** G. B. S. Salaria (Chem. Lab., Univ. of Allahabad, India). *Anal. Chim. Acta*, 1959, **20** (1), 68–69.—Ruthenium and In can be quant. separated from the alkaline-earth metals by methods similar to those described previously (*Anal. Abstr.*, 1959, **6**, 2459). The sample soln. is treated with aq. NH_3 until a turbidity appears and then 2 *N* Na_2S, acetic acid and solid ammonium acetate are added. After boiling and cooling the mixture, the pptd. sulphide is filtered off, washed, dried and weighed. Ruthenium is recovered with an accuracy of $+0·14$ to $-0·33$% and In with an accuracy of $+0·29$ to $-0·24$%.

IX. Separations of alkaline-earth metals from some elements that form thio salts. I. K. Taimni and S. N. Tandon (Chem. Lab., Univ. of Allahabad, India). *Ibid.*, 1959, **20** (1), 70–72.—Arsenic, Sb, Te, Se and Mo can be quant. separated from Ca, Sr and Mg by adding excess of 2 *N* Na_2S and then acidifying with HCl. After boiling and cooling the mixture, the pptd. sulphide can be filtered off. Results are quoted for the analysis of a series of synthetic mixtures. The method cannot be applied to Sn because the ppt. of SnS_2 peptises on being washed. W. T. CARTER

3406. **Rapid determination of beryllium oxide in beryllium metal.** A. R. Eberle and M. W. Lerner (U. S. Atomic Energy Comm., New Brunswick Lab., N.J.). *Metallurgia, Manchr*, 1959, **59**, 49–52.—The method is based on that for the determination of oxide in aluminium. After selective dissolution of the metal in soln. of Br - methanol and HCl - methanol, BeO in the undissolved residue is analysed for Be by the conventional *p*-nitrophenylazo-orcinol method or, alternatively, by the addition of NaF and excess of 0·05 *N* H_2SO_4, followed by back-titration with 0·05 *N* NaOH. The method compares favourably with the HCl volatilisation procedure. J. W. O. PYEMONT

3407. **Rapid radiometric determination of magnesium.** Atsushi Mizuike, Toshihiro Nakajima and Shizo Hirano (Inst. of Techno-anal. Chem., Fac. of Engng, Tokyo Univ., Hongo). *Japan Analyst*, 1958, **7** (9), 588–590.—Magnesium (<20 mg) is pptd. with $(NH_4)_2HPO_4$ labelled with ^{32}P and the radioactivity of the supernatant liquid is measured with a Geiger - Müller counter of the immersion type. Good agitation is essential for obtaining reproducible results. There is no interference from $<M$ NH_4Cl, <200 mg (per 60 ml) of NaCl, <100 mg of KCl and <50 mg of ammonium oxalate per 2 mg of Mg. K. SAITO

3408. **Improved 8-hydroxyquinoline method for the determination of magnesium oxide in Portland cement.** H. A. Berman (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *Bull. A.S.T.M.*, 1959, (237), 51–55.—The U.S. Federal and A.S.T.M. optional rapid volumetric methods (dissolution of Mg oxinate in hot HCl, addition of $KBrO_3$ - KBr and KI, followed by titration with $Na_2S_2O_3$) give high values, poor reproducibility and too many "specification" failures. Greater accuracy and reproducibility are attained by a double pptn. of Mg oxinate; the amount of oxine added is independent of the content of MgO, which had to be known approx. in the old method. The error is $\pm0·03$% for 2 to 5% of MgO; when determining lower concn. a known amount of MgO (as $MgCl_2$) is added to bring the concn. within the upper range. For cements high in Mn_2O_3, a preliminary removal of Mn is necessary. The improved procedure is recommended to replace the present referee method (determination as $Mg_2P_2O_7$). W. J. BAKER

3409. **Detection of calcium ion.** H. Weisz (Inst. f. anorg. u. allg. Chem., Tech. Hochsch., Vienna). *Mikrochim. Acta*, 1959, (1), 32–35.—Calcium ions react with a soln. containing Zr^{4+} and alizarin red S (**I**) which has been decolorised by addition of F^-, combining with F^- and liberating Zr^{4+} to react with **I**. Interference by Ba^{2+} and Sr^{2+} is overcome by their prior conversion into sulphates. *Procedure*—Dissolve 0·1 g of **I** in 100 ml of water and add 20 drops of $ZrO(NO_3)_2$ soln. (0·2%). Add dropwise NaF soln. (1%) till the red - violet colour is just discharged. The resulting soln. is stable. Treat the mixed carbonates, or an acetic acid soln., with 1 drop of H_2SO_4 (2 *N*) and evaporate to dryness. Cool, and add 1 drop of reagent soln. A red - violet colour within 1 to 3 min. indicates Ca^{2+}. As little as 1 μg of Ca has been detected. T. R. ANDREW

3410. **The sucrose-extraction method of determining available calcium oxide in hydrated lime.** D. R. Moorehead and W. H. Taylor (Div. Building Res., C.S.I.R.O., Highett, Victoria, Australia).

Bull. A.S.T.M., 1959, (236), 45–47.—The validity of the sucrose-extraction method for determining free CaO in hydrated and high-CaO limes is confirmed; satisfactory results are obtained in a fraction of the time required for a total analysis. The accuracy is unaffected by the amount of MgO present, but it does depend on the size of the sample. Optimum conditions for accuracy are—a sample of $\geq 0{\cdot}6$ g shaken for 15 min. in 10% sucrose soln. (100 ml) and then titrated with N HCl at 21°, followed by re-titration at the boiling-point to ensure complete hydrolysis of the sucrate.

W. J. BAKER

3411. **Complexometric titration method for determining calcium in the presence of magnesium.** A. Ringbom, G. Pensar and E. Wänninen (Dept. of Anal. and Inorg. Chem., Åbo Akad., Finland). *Anal. Chim. Acta*, 1958, **19** (6), 525–531.—The 'conditional' formation constants for complexes of Ca^{2+}, Mg^{2+} and Zn^{2+} with 1:2-di-(2-aminoethoxy)-ethane-NN′-tetra-acetic acid (**I**) have been studied in the pH range 4 to 13, and that for the Zn-zincon complex in the range 6 to 13. The effect of varying the concn. of NH_4^+ is reported. It is shown that Ca may be titrated with **I** at pH 9·5 to 10·0 in the presence of Mg, with 2 ml of a soln. of the zinc salt of **I** (0·025 M) and 2 drops of 0·065% zincon in 0·002 N NaOH as indicator, in a borate buffer at an NH_4^+ concn. of 0·02 to 0·05 M.

T. R. ANDREW

3412. **Flame-photometric determination of calcium in silicate rocks.** M. Stone and J. E. Thomas (Dept. of Geology, Univ. Coll., Keele, Staffs., England). *Analyst*, 1958, **83**, 691–694.—The powdered dried rock (0·2 g) is heated with HF and H_2SO_4 on a water bath until digestion is complete. The digest is heated to fuming, cooled, diluted with water and digested on the water bath for $\simeq$ 30 min. If insol. matter is present the liquid is then boiled and any remaining insol. matter is examined for Ca-containing minerals with a petrological microscope. The cooled soln. is adjusted to the yellow end-point of methyl red with dil. aq. NH_3, then centrifuged, and the supernatant liquid is decanted into a 50-ml flask (a double pptn. of R_2O_3 is usually necessary) and adjusted to the mark with 0·5 N H_2SO_4. The Ca content is then determined in the flame photometer with the zero set against 0·5 N H_2SO_4 and full-scale deflection with the appropriate standard soln. Quoted results indicate satisfactory accuracy.

A. O. JONES

3413. **Application of selective adsorbent resin to analytical chemistry. I. Separation and determination of calcium and magnesium in a concentrated solution of sodium chloride.** Toshiharu Takagi and Hiroshi Imoto (Toyo Soda Mfg Co., Tonda, Yamaguchi-ken). *Japan Analyst*, 1958, **7** (9), 565–568.—A special resin having a chelating action towards Mg and Ca was prepared from Amberlite IR-4B by the action of NaOH and chloroacetic acid (**I**). The rate of exchange between adsorbed Na and free Ca or Mg is very slow, and only the batch method can be used. By agitation for 30 min., both Ca and Mg (<5 mg) are quant. adsorbed by the resin (10 g) from NaCl (<5 M) and are eluted with 50 ml of 0·5 N HCl within 10 min. Interfering ions, including Fe^{3+} and Al^{3+}, can be removed by extracting their oxinates with $CHCl_3$ from a neutral soln. (pH 7, adjusted with 5% $NaHCO_3$ soln.). *Procedure*—Treat Amberlite IR-4B (15·12 g) with NaOH soln. (9%, 1670 g) and **I** (150 g) at 60° to 70° for 17 hr.; wash and dry the product. Add this resin (10 g) to the sample soln. and stir the suspension for 30 min. at room temp. Filter off the resin, wash with water and stir with HCl (0·5 N, 50 ml) for 10 min. Filter the soln. into a measuring flask (250 ml) and use a 100-ml portion for the EDTA titration of Ca [2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid as indicator] (*cf. Anal. Abstr.*, 1956, **3**, 2982) and of the sum of Ca and Mg (Eriochrome black T).

K. SAITO

3414. **Complexometric determination of calcium and magnesium in cements.** D. Deur-Šiftar and E. Bauman (Zavod za anorg. Tehnol. i Metalurg., Zagreb, Yugoslavia). *Kem. i Ind., Zagreb*, 1959, **8** (1), 1–7.—*Procedure*—A sample (1 g) of cement is boiled with 15 ml of H_2O and 30 ml of conc. HCl, then cooled to 70° and treated with 1% gelatin soln., added dropwise. The ppt. is filtered off after 10 min., then washed and ignited to give SiO_2. The filtrate can be treated with bromine water and aq. NH_3 for the pptn. of $Al(OH)_3$ and $Fe(OH)_3$, or the Al and Fe can be masked with triethanolamine. The filtrate is then made up to 500 ml and 50-ml aliquots are taken for the determination of Ca and Mg with EDTA.

A. GROCHOWSKI

3415. **Rapid and accurate automatic titration of calcium and magnesium in dolomites and limestones. Use of EDTA titrant and automatic derivative spectrophotometric end-point determination.** H. V. Malmstadt and T. P. Hadjiioannou (Dept. of Chem. and Chem. Engng, Univ. of Illinois, Urbana, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (6), 563–569.—By utilising an automatic derivative spectrophotometric titrimeter (*cf. Anal. Abstr.*, 1957, **4**, 4209) Ca may be determined in the presence of Mg by EDTA titration at pH 13, with calcon as indicator. Total Mg plus Ca is determined at pH $\simeq$10 with Eriochrome black T as indicator. Results are reported in the ranges 0·2 mg to 2·0 mg for Mg and 1·0 to 4·0 mg for Ca. The time required for both determinations is <5 min.

T. R. ANDREW

3416. **Limestone for making colourless glasses.** British Standards Institution (2 Park Street, London). B.S. 3108: 1959, 15 pp.—Sampling methods are given, and apparatus and procedure specified for the following determinations—moisture, size-grading, inspection for magnetic materials and carbonaceous matter, qual. analysis, non-volatile matter insoluble in HCl, Al, Ca, Mg, iron oxide, and organic matter.

H. M.

3417. **Detection of barium and strontium in a drop.** H. Weisz (Inst. f. anorg. u. allg. Chem., Tech. Hochsch., Vienna). *Mikrochim. Acta*, 1959, (1), 29–31.—The test drop is absorbed on filter-paper and treated with Na rhodizonate soln. (0·1%). A red-brown stain indicates Ba or Sr or both. Wash twice with acetic acid (1:2) to remove excess of reagent, and add one drop of $AgNO_3$ soln. (1%) and one drop of acetic acid (1:2). In the presence of Sr a blue-violet fleck appears. A spot of ammonium oxalate soln. (2%) is added and the test spot is held over conc. aq. NH_3. The colours due to Ag and Sr rhodizonates and free rhodizonic acid disappear, while the red Ba rhodizonate is unaffected.

T. R. ANDREW

3418. **Flame-photometric determination of small amounts of barium.** M. Dzubay (Agric. Expt. Inst., Délalföld, Szeged, Hungary). *Magyar Kém.*

Foly., 1958, **64** (12), 483–484.—The determination of Ba in 0·01 to 0·001 *M* $BaCl_2$ soln. at 770 mμ, in the presence of large amounts of Ca, is described. As both Ca and Mg give a slight emission at this wavelength, the sample and standard soln. are adjusted to contain 2·5% of $CaCl_2.2H_2O$ and of $MgCl_2.2H_2O$. The coeff. of variation for 9 measurements is ±0·72% and for a single measurement is ± 2·05%. G. SZABO

3419. **Decomposition of barium sulphate with hydrogen chloride and determination of the barium by titration of the chloride formed.** J. Agterdenbos, Y. C. de Wijs and J. E. Ordelman (Univ. of Amsterdam, Holland). *Z. anal. Chem.*, 1959, **165** (6), 421–423.—Barium sulphate is quant. decomposed by heating at 1000° in HCl gas, and the Ba can be indirectly measured by potentiometric titration, with $AgNO_3$, of the chloride formed. Analysis of 6 standards showed a mean decomposition of 100% with a standard deviation of ±0·9%. At 1100°, recovery of Cl^- is low owing to its volatility at this temp. The method is often applicable to impure $BaSO_4$. G. P. COOK

3420. **Separation of strontium-90 and yttrium-90 by the use of an anion-exchange resin in the oxalate form.** Seishi Yajima, Eiji Shikata and Chizuko Yamaguchi (Japan Atomic Energy Res. Inst., Tokai, Ibaragi-ken). *Japan Analyst*, 1958, **7** (11), 720.—Carrier-free ^{90}Sr in 1% ammonium oxalate soln. of pH 2 to 7 passes through a column (diam. 6 mm, length 10 cm) of Dowex 1-X7·5 (50 to 100 mesh) (oxalate form), but ^{90}Y is adsorbed and can be eluted with 0·5 *N* HCl. A similar result was obtained by the use of 0·5% NH_4Cl soln. (pH 2 to 6) in place of the oxalate soln. K. SAITO

3421. **Electrochromatography in the separation of ions. VI. Separations of zinc-group metals.** A. K. Majumdar and B. R. Singh (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1958, **19** (6), 520–522.—In KCN soln., at pH 6, a quaternary mixture of Ni, Zn, Co and Mn may be resolved by electrochromatography. No success was obtained with quaternary mixtures in 30 other electrolytes studied. T. R. ANDREW

3422. **Determination of cadmium in zinc anodes.** W. C. G. Wheeler and D. Durant (Central Dockyard Lab., H. M. Dockyard, Portsmouth, England). *Metallurgia, Manchr*, 1959, **59**, 53–54.—Cadmium with some Zn is removed as sulphide from the H_2SO_4 soln. The Zn is separated with an NH_4Cl - phosphate soln. and the Cd finally determined colorimetrically as the sulphide. J. W. O. PYEMONT

3423. **Extraction and flame-spectrophotometric determination of aluminium.** H. C. Eshelman, J. A. Dean, O. Menis and T. C. Rains (Dept. of Chem., Univ. of Tennessee, Knoxville, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 183–187.—Selective extraction with a chelating agent (2-thenoyltrifluoroacetone or cupferron) in 4-methylpentan-2-one can be used to isolate Al from many elements. The organic phase can then be aspirated directly into an oxy-acetylene or oxy-hydrogen flame with a 100-fold increase in sensitivity compared with a similar aq. soln. The calibration curve is linear from 5 to 40 μg of Al per ml. The effect of a wide variety of ions has been studied. Procedures for the preliminary separation from large amounts of interfering elements are outlined. K. A. PROCTOR

3424. **Colorimetric determination of aluminium in heat-resistant alloys.** H. Zibulsky, M. F. Slowinski and J. A. White (Austenal Inc., Dover, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 280–281.—After dissolution of the alloy, a double cupferron - $CHCl_3$ separation leaves Al in the aq. phase. Complexing agents are added, followed by 8-hydroxyquinoline and the aluminium 8-hydroxyquinolinate formed is extracted with $CHCl_3$. Three extractions are necessary. The extracts are made up to 100 ml and the extinction of the soln. is measured at 380 mμ or 425 mμ against a reagent blank. Satisfactory results are claimed for steels and nickel-base alloys containing up to 7% of Al. In the suggested procedure, only U, Mg, Mn and rare-earth elements cause serious interference. F. L. SELFE

3425. **Photometric determination of aluminium and titanium in polyethylene.** W. T. Bolleter (Monsanto Chem. Co., Texas City, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 201–203.—Wet- and dry-ashing procedures for the decomposition of polyethylene samples are described. The soln. obtained by either procedure is diluted to 100 ml and separate aliquots are taken for the Al and Ti determinations. *Procedure for aluminium*—The aliquot is treated to give aluminium 8-hydroxyquinolinate, and the complex is extracted into 10 ml of trichloroethylene. The extinction of the extract is measured at 390 mμ against a reagent blank. The optimum concn. range is from 5 to 30 μg of Al per 10 ml of solvent for a 1-cm cell. The system conforms to Beer's law over this range, and Al can be determined to within ±0·2 μg. Results are quoted for the extent of interference by Ti, V, Zr, Fe, Mo, Ni, Cu, Zn and Cr. *Procedure for titanium*—The aliquot is treated to give the coloured Ti complex with chromotropic acid, adding EDTA (disodium salt) to remove the green iron - chromotropic acid complex. The extinction of the soln. is measured at 420 mμ against a reagent blank. The optimum concn. range in the final soln. is 0·4 to 2·5 p.p.m. for a 1-cm, and 0·08 to 0·5 p.p.m. for a 5-cm, cell. Results are quoted for the extent of interference due to Zr, Cr, Fe, V, Cu, Mo, Ni, Zn, Al and NH_4^+. The standard deviation for the determination of each metal is ±1 in the range 5 to 50 p.p.m. F. L. SELFE

3426. **Volumetric determination of aluminium and ferric iron with EDTA with the use of Chrome azurol S and o-dianisidine as indicators.** Tsutomu Matsuo (Fac. of Liberal Arts and Sci., Univ., Koshirakawa-cho, Yamagata). *Japan Analyst*, 1958, **7** (9), 557–560.—The indication of the end-point for the EDTA titration of Al^{3+} at pH 4 (phthalate buffer) with Chrome azurol S (C. I. Mordant Blue 29) (**I**) is not sharp. Ferric iron is satisfactorily titrated at pH 4 with *o*-dianisidine or at pH 2 with **I** as indicator. Differential titration (indicator **I**) at pH 2·0 (for Fe) and 4·0 (for Al) always gives low values for Al. K. SAITO

3427. **Metallurgical polarographic analysis. V. Rapid determination of copper and iron in aluminium and its alloys.** Yoshiaki Miura (Yawata Iron and Steel Works, Fukuoka-ken). *Japan Analyst*, 1958, **7** (11), 699–702.—*Procedure*—Dissolve the sample (0·5 g) in NaOH (5 *N*, 20 ml), add warm water (80 ml) and Na_2S soln. (20%, 5 ml) and warm at 50° for 30 min. Filter off the ppt., wash with 2% Na_2S soln. and dissolve the residue in HNO_3 (1:1, 10 ml) and aq. bromine soln. (a few ml). Evaporate to <5 ml, neutralise with 5 *N* NaOH and add ethylenediamine tartrate soln. (2 *M*, 12·5 ml),

$K_4P_2O_7$ soln. (1 *M*, 5 ml) and water to a total vol. of 50 ml. Measure the limiting current at −0·35 V (for Cu) and −0·60 V (for Fe) *vs.* the S.C.E. The results agree well with those obtained by conventional methods and the time taken for a determination is <90 min. K. SAITO

3428. Fluorimetric determination of gallium with Eriochrome red B. Yasuharu Nishikawa (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku). *Japan Analyst*, 1958, **7** (9), 549–552.—The fluorimetric detection of Ga (*cf.* Wiebush, *Anal. Abstr.*, 1956, **3**, 2961) was applied to its quant. determination. The intensity of the fluorescence (max. 490 mμ) is strongest at pH 3 to 3·9; it increases in the presence of ammonium acetate soln. (optimum 10%, 2 ml per 50 ml) and remains unchanged for 2 hr. The working curve is linear for <10 μg of Ga per 50 ml. Interference resulting from Fe^{III}, Tl^{III}, VO_3^-, WO_4^{2-} and MoO_4^{2-} is masked with hydroxyammonium chloride; Al, Cu and Th give similar colorations; Ga is separated by extraction with diethyl ether. The sample soln. is mixed with Eriochrome red B (C. I. Mordant Red 9) soln. (0·1%, 0·4 ml) and ammonium acetate soln. (10%, 2 ml), the pH is adjusted to 3·2 with *N* H_2SO_4, the whole is diluted to 50 ml and heated on a water bath for 10 min. The fluorescence is measured with quinine sulphate (0·08 μg per ml of *N* H_2SO_4) as standard. K. SAITO

3429. Complexometric titration of gallium with fluorescent indicator. R. H. A. Crawley (B.T.-H. Res. Lab., Rugby, England). *Anal. Chim. Acta*, 1958, **19** (6), 540–541.—Evaporate the gallium soln. to about 5 ml, add 5 ml of K H phthalate soln. (4%) and adjust the pH to 2·5 to 3·5. Add 1 ml of hydroxyammonium chloride soln. (20%) and 1 ml of 8-hydroxyquinoline soln. (0·05% in 0·5% acetic acid) and titrate with 0·001 *M* EDTA (disodium salt); u.v. irradiation is used to detect the end-point (disappearance of fluorescence). The range is 50 to 1000 μg of Ga; for amounts of <50 μg, errors were too large for the method to be of practical use. T. R. ANDREW

3430. Determination of thallium by a dithizone mixed-colour method. R. S. Clarke, jun., and F. Cuttitta (U.S. Geological Survey, Washington, D.C.). *Anal. Chim. Acta*, 1958, **19** (6), 555–562.—Thallium is extracted by a $CHCl_3$ soln. of diphenylthiocarbazone (**I**) (0·008%) (15 ml) from a soln. containing Na citrate (5 ml of 25% soln.), Na_2SO_3 (1 ml of 5% soln.) and KCN (2 ml of 5% soln.) in a total vol. of 20 ml. The extract [together with washings with $CHCl_3$ (2 × 3 ml)] is shaken with HNO_3 (15 ml of 0·08 *N*). The aq. layer is retained and neutralised to methyl red with NaOH soln. (0·08 *N*); KCN (2 ml of 5% soln.) is added, followed by **I** soln. (15 ml of 0·0027% in $CHCl_3$) and the $CHCl_3$ extract is measured at 505 mμ against pure $CHCl_3$. The range is up to 100 μg of Tl; Pb, Bi and Sn^{II} interfere. T. R. ANDREW

3431. EDTA titration of micro quantities of rare earths. K. L. Cheng (Metals Div., Kelsey Hayes Co., Utica, N.Y., U.S.A.). *Chemist Analyst*, 1958, **47** (4), 93–94.—The method has been used for the indirect titration of all the rare-earth metals (except radioactive Pm) in the tervalent state, in the pH range 4 to 10, with 1-(2-pyridylazo)-2-naphthol as indicator. To a 15- or 25-ml porcelain dish add a suitable aliquot of 0·001 *M* rare-earth-metal soln., a slight excess of 0·001 *M* EDTA and a few crystals of sodium or ammonium acetate. Adjust to a pH between 4 and 10 with acetic acid or aq. NH_3, add 1 to 2 drops of 0·1% methanolic indicator soln. and 2 to 3 ml of methanol, and back-titrate the excess of EDTA with 0·001 *M* $CuSO_4$ till the colour changes from yellow to reddish brown. Correct the result by a reagent blank. Diethylenetriaminepenta-acetic acid is as satisfactory as EDTA for this titration. The pH should be above 3, but as low as feasible, to attain higher selectivity. At pH 5 to 6, Ce^{IV} cannot be titrated satisfactorily, but it can be reduced to Ce^{III} with ascorbic acid, when the titration is satisfactory at pH 5 to 10; the excess of ascorbic acid does not interfere. Cupferron is not satisfactory as a masking agent in the titration of mixtures of rare-earth metals, as an excess interferes with the end-point. R. E. ESSERY

3432. Rapid analytical methods for metals and minerals. VII. Polarographic determination of cerium in alloys and minerals. J. Doležal and J. Novák (Inst. Anal. Chem., Charles' Univ., Prague). *Chem. Listy*, 1958, **52** (11), 2060–2065.—Results obtained in studying the polarographic behaviour of Ce in soln. of K_2CO_3 and K Na tartrate (*Chem. Listy*, 1958, **52**, 582) have been applied to the determination of Ce in various materials. The method is suitable for the determination of 1% of $Ce^{\cdot}$ in iron and zinc, 3% in aluminium, 5% in vanadium and nickel, 0·1% in thorium and uranium, 0·5% in yttrium, and 5% in scandium; the presence of large amounts of Bi, Cr^{3+}, Ti, Pb, Cd, Mg, Mo, W, Pr, Nd, Sm, Gd and Er causes no interference. *Procedure for alloys containing Th, Al and Mg*—Dissolve the sample containing about 5% of Ce (0·5 to 1 g) in a mixture of HNO_3, HCl and H_2O (3:1:6) (20 ml) by heating in a porcelain dish, evaporate to dryness, add HNO_3 (1:2) (1 ml) and H_2O (30 ml) and heat till dissolution is complete. Transfer the soln. to a 100-ml flask, mix, make up to volume and transfer 5 ml to a 25-ml flask. Remove O by bubbling with N (5 min.), add saturated soln. of K Na tartrate (5 ml) and K_2CO_3 (8 ml), mix, make up to volume, transfer immediately to a polarographic vessel, remove O by bubbling with N for 5 min. and record the wave from +0·1 V *vs.* the S.C.E. Evaluate the results by the method of standard additions. *Procedure for Ce in monazite*—Fuse the finely powdered sample (0·5 g) with Na_2O_2 (5 g), cool and dissolve in H_2O. Filter off the pptd. hydroxides on paper, wash with 0·1 *N* KOH, ignite and fuse the residue with NaOH (0·5 to 1 g). Cool, add Na_2O_2 (5 to 8 g), repeat the fusion and filtration, wash with 0·1 *N* KOH (20 ml), take up the ppt. in HNO_3 (1:4) (20 ml), filter, add to the filtrate H_2O_2 (30%) (3 drops) and heat till the yellow colour is discharged. Transfer to a 100-ml flask, add *M* KOH till a ppt. of hydroxides is formed, add conc. HNO_3 (5 drops) and dilute with H_2O to vol. Take 5 ml of this soln. and proceed as described above. J. ZÝKA

3433. The separation of fission products. III. Separation of carrier-free praseodymium-144 by extraction from cerium-144. Masuo Yagi (Fac. of Educ., Shizuoka Univ., Oiwa-cho). *Japan Analyst*, 1958, **7** (12), 775–778.—Cerium-144, pptd. with carrier Ce as iodate by the usual method, is mixed with glass wool and placed in an ice-cooled column (diam. 10 mm, height 15 mm). When this column is eluted with HNO_3, ^{144}Pr is eluted together with Ce and the amount of Ce increases with increase in concn. of HNO_3. However, by the use of concn.

$<0{\cdot}005$ *N* (rate of flow, 3 ml per min.), the amount of Ce eluted is negligible; the radiochemical purity is $\simeq 97\%$. K. Saito

3434. Extraction and flame-spectrophotometric determination of lanthanum. O. Menis, T. C. Rains and J. A. Dean (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 187–191.—Lanthanum can be selectively extracted with 2-thenoyltrifluoroacetone in 4-methylpentan-2-one from a buffered solution (pH 5) and then determined by flame photometry. Of several emission bands, that at 743 mμ is the most suitable for measurement. The effect of a number of interfering elements has been studied: of these only Ti and Al interfere when they are present in greater amounts than the La. Fluoride and phosphate interfere by preventing the extraction of the La. K. A. Proctor

3435. Suppression of cyanogen bands for the spectrographic analysis of erbium oxide. E. M. Hammaker, G. W. Pope, Y. G. Ishida and W. F. Wagner (Dept. of Chem., Univ. of Kentucky, Lexington, U.S.A.). *Appl. Spectroscopy*, 1958, **12** (6), 161–163.—The suppression of cyanogen bands from d.c. arc spectra by using atmospheres of A, He and CO_2 with or without O has been investigated. Working curves for the determination of Dy, Tm and Ho in erbium oxide have been prepared from spectra of samples arced in an atmosphere of 80% of A and 20% of O. Cyanogen bands were eliminated and the background intensity reduced so that sensitive lines could be used for the determination. K. A. Proctor

3436. Photometric determination of silicon as α-molybdosilicic acid. A. Ringbom, P. E. Ahlers and S. Siitonen (Dept. of Anal. and Inorg. Chem., Åbo Akad., Finland). *Anal. Chim. Acta*, 1959, **20** (1), 78–83.—The observations of Strickland (*J. Amer. Chem. Soc.*, 1952, **74**, 862, 868, 872) on the formation of α- and β-molybdosilicic acids have been utilised to develop an accurate colorimetric method for silicon in rocks and other silicate materials. *Procedure*—Fuse the sample (0·1 to 0·3 g) containing up to 70% of SiO_2 with NaOH (10 g) in a nickel crucible. Dissolve the melt in water containing 0·05 *M* EDTA (disodium salt) (40 ml) and dilute to 500 ml. Pipette a suitable aliquot into a flask containing ammonium molybdate soln. [35·3 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ per litre] (10 ml) and sufficient chloroacetic acid - ammonium chloroacetate buffer to give a pH of 3·0 to 3·7. Heat in boiling water for 5 to 10 min., dilute to 50 ml and measure the extinction at 390 mμ. The effects of pH, concn. of molybdate and the interference caused by P, Ge and As have been studied. Results are given for a series of standard samples. W. T. Carter

3437. Simple determination of silicon as a non-metallic inclusion in weld metal. Shuichiro Mizoguchi and Tadaji Oguma (Toyo Denkyoku Kogyo Co., Hiratsuka-cho, Shinagawa-ku, Tokyo). *Japan Analyst*, 1958, **7** (9), 586–587.—The amount of Si as non-metallic inclusion is determined by deducting the Si content measured by the colorimetric method from that by the gravimetric. The results agree well with those by the electrolytic method. K. Saito

3438. Polarographic determination of tin in the presence of dichromic acid. J. Šára (Res. Inst. Electrotech. Physics, Prague). *Chem. Průmysl*, 1958, **8** (12), 636–637.—Citric acid has been found to be the most suitable agent for the reduction of dichromic acid (**I**) and for the removal of its interfering influence in the polarographic determination of Sn in the presence of **I** as well as of other oxidising agents (peroxide, bromate, persulphate, permanganate). The total amount of Sn can be determined whatever its valency. *Procedure*—To 5 ml of the soln., containing $\geqslant 1$ millimole of Sn in 1 ml, add 5 ml of a soln. of citric acid (**II**) (52·5 g of **II**, 53·5 g of NH_4Cl and 154 ml of conc. HCl, diluted to 250 ml), heat till green or blue - green, and cool. Add gelatin soln. (0·1%) (3 drops) and dilute to 50 ml with a soln. of 4 *N* NH_4Cl which is *N* in HCl. Transfer to a polarographic vessel, remove O with N and register the wave from $-0{\cdot}2$ to $-0{\cdot}8$ V. Evaluate by the method of standard additions. Measure the height of the wave at $-0{\cdot}56$ V. If As, Sb, Pb, Cu or Bi is present, the soln. is oxidised with $KMnO_4$ and determined after reduction with **II**. Results are precise to within ±3%. J. Zýka

3439. Metallurgical polarographic analysis. VI. Rapid determination of tin(IV) and lead. Analysis of solders. Yoshiaki Miura (Yawata Iron and Steel Works, Fukuoka-ken). *Japan Analyst*, 1958, **7** (12), 779–782.—By using 4 *M* NH_4Br as supporting electrolyte (Lingane *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 919), Sn^{IV} gives two waves at $-0{\cdot}22$ and $-0{\cdot}56$ V *vs.* the S.C.E., the second overlapping the Pb wave at $-0{\cdot}56$ V. The amount of Sn is determined from the height of the first wave and that of Pb calculated from the height of the second wave. There is no interference from HCl (<1 *N*), Cd, As, Zn, and small amounts of Cu, Fe, Bi and Sb. The results agree with those obtained by conventional methods and the time taken for a determination is <40 min. K. Saito

3440. Ultra-violet spectrophotometric determination of lead with perchloric acid. Masayoshi Ishibashi, Yuroku Yamamoto and Kazuo Hiiro (Chem. Dept., Kyoto Univ., Sakyo-ku). *Japan Analyst*, 1958, **7** (9), 582–585.—Lead perchlorate exhibits an absorption at 208 mμ at pH $<3{\cdot}4$ and the extinction is proportional to the amount of Pb (<20 p.p.m.) at a given pH; in alkaline soln. the absorption at 208 mμ disappears and another one appears at 240 mμ, the extinction markedly changing with time. Ferric iron (>1 p.p.m. for 10 p.p.m. of Pb), Sn^{4+} (>20 p.p.m.), Sb^{5+} and Bi give similar colorations and interfere. The range for colorimetry is increased by the use of a differential method with *N* $HClO_4$ containing 40 p.p.m. of Pb as reference, and by measuring the extinction at 218 mμ. K. Saito

3441. Determination of bivalent and tervalent titanium in chloride melts by means of ferric chloride. L. E. Ivanovskiĭ, N. A. Loginov and M. V. Smirnov (Inst. Chem., Ural Branch of Acad. Sci. USSR, Sverdlovsk). *Zhur. Anal. Khim.*, 1958, **13** (6), 671–673.—Cool a suitable sample in an inert atmosphere (argon) and transfer it into a test-tube fitted with a side arm. Introduce into the side-arm enough previously prepared $KFeCl_4$ (pure $FeCl_3$ fused at 450° to 500° with a eutectic mixture of KCl and LiCl in a current of Cl) for the complete oxidation of Ti^{2+} and Ti^{3+} to Ti^{4+}. Fill the tube with pure argon and place the lower part, containing the sample, in a hot oven. The side-arm must be in a cold zone outside the oven. When the sample has melted, tilt the tube so that $KFeCl_4$

is introduced into the melt. Shake vigorously, remove the tube from the oven and cool it as soon as possible to room temp. Weigh the sample, dissolve it in dil. (10%) H_2SO_4 or HCl and determine Fe^{II}. Take another sample melt and, after cooling it to room temp. in an inert atmosphere (argon), dissolve it in dil. (10%) H_2SO_4 or HCl and determine Ti^{III}. If n = milli-equiv. of Fe^{3+} for 1 g of sample fused with $FeCl_3$, and m = milli-equiv. of Ti^{3+} for 1 g of sample in aq. soln., then the analysed salt melt contains $11{\cdot}88\ (n - m)$ % (w/w) of $TiCl_2$ and $15{\cdot}43\ (2m - n)$ % (w/w) of $TiCl_3$.

W. Roubo

3442. Rapid determination of chlorine in titanium. Nakaaki Oda and Masaji Kubo (Takaoka Plant, Nippon Soda Co., Toyama-ken). *Japan Analyst*, 1958, **7** (11), 707–711.—Various methods for the determination of Cl in metallic titanium were examined for their suitability in routine analysis. No loss of Cl takes place when <30 ml of HF (46%) is used for 5 g of the sample (20 to 30 mesh) containing $\simeq$ 0·05% of Cl. Other conditions, including the amount of HNO_3 (oxidant for Ti) and $AgNO_3$ and the time for digestion of AgCl, were also examined. The error is $\simeq 5\%$ for $>0{\cdot}05\%$ of Cl. *Procedure*—Dissolve the sample (5 g) in HF (46%, 20 ml in 3 portions) add H_3BO_3 soln. (10%, 50 ml) and HNO_3 (20 ml) and stir until the soln. becomes colourless. Filter, if necessary, and add $AgNO_3$ soln. (5%, 10 ml) and centrifuge (3000 r.p.m.) for 10 min. Keep the product in the dark for 30 min. and filter off the ppt. on asbestos, wash with 1% HNO_3 and water and dry at 130° in a current of filtered air.

K. Saito

3443. Analytical aspects of some organic acids. I. Gravimetric determination of zirconium by *o*-phenylenedioxydiacetic acid. C. S. Pande and T. S. Srivastava (Chem. Dept., Univ., Lucknow, India). *Z. anal. Chem.*, 1959, **165** (1), 11–16 (in English).—Zirconium (>2 mg) is quant. pptd. from 0·1 to 0·4 *N* HCl by *o*-phenylenedioxydiacetic acid (**I**). The ppt. is of variable composition and must be ignited to ZrO_2 before weighing. In the determination of 42 mg of ZrO_2, Ca (296 mg), Ba (375), Zn (161), Hg^{2+} (373), Al (213), Ce (167), Ti (137), Th (187), UO_2^{2+} (206), Mn^{2+} (164), Fe^{3+} (283), Co (326) and Ni (324) do not interfere. Contamination of the ppt. by $V_2O_4^{4+}$ (162 mg) and Cr^{3+} (139 mg) is eliminated by double pptn.; SO_4^{2-} (threefold excess) do not interfere. Results for the determination of 42 mg of ZrO_2 are accurate to within $\pm 0{\cdot}5\%$. *Procedure*—To a boiling aliquot (2 to 100 mg of Zr) add NH_4NO_3 (5 g per 100 ml) and, slowly with stirring, hot 2% aq. **I**. Adjust the acidity of the soln. to 0·3 *N* in HCl. Collect the ppt., wash it with hot 0·1% **I** soln., and ignite to ZrO_2.

J. P. Stern

3444. Volumetric determination of zirconium. I. Titration in alkaline medium with potassium permanganate. A. Schneer and H. Hartmann (Dept. of Gen. and Inorg. Chem., L. Eötvös Univ., Budapest). *Magyar Kém. Foly.*, 1959, **65** (1), 31–36.—A method has been developed for the determination of mandelic acid (**I**) and *p*-bromomandelic acid with $KMnO_4$ in alkaline medium, and is applied to the determination of Zr. *Procedure*—Concentrate the HCl soln., containing Zr (2 to 20 mg) and any other cation, to 20 to 100 ml, depending on the total concn. Add conc. HCl (15 to 80 ml) and precipitate Zr at 95° by adding dropwise, with stirring, a 16% soln. of **I** (15 to 80 ml). Heat the mixture on a water bath for a few hours, with occasional stirring, and then set aside at room temp. overnight. (If 0·2 to 0·4 mg of Zr is present, keep for 2 days and, if $\simeq$0·1 mg of Zr is present, keep for 3 days.) Collect the Zr tetramandelate on a 10G4 glass filter and wash with the mother liquor of a soln. from which the only cation, Zr, has been pptd. with **I**. Transfer the last traces of the ppt. to the filter with ethanol, wash with ethanol (3×10 ml) and diethyl ether (2×10 ml) and dry. Dissolve the ppt., with suction, at $\simeq$60° with 5 *N* to 6 *N* Na_2CO_3 (4×5 ml) and wash the filter with H_2O (10 to 15 ml). Add 23% (w/w) NaOH soln. (10 ml) and 0·5 *N* $KMnO_4$ (20 ml). After 10 min., add H_2O (250 to 300 ml), $\simeq 50\%$ (w/w) H_2SO_4 (20 ml) and 0·5 *N* oxalic acid (**II**). Warm the soln. to 60° and back-titrate the excess of **II** with 0·1 *N* $KMnO_4$. Carry out a blank; the difference between the two $KMnO_4$ titrations gives the wt. of Zr present. It was found that 1 ml of 0·1 *N* $KMnO_4$ = 0·5136 mg of Zr. The error is $<\pm 1\%$.

A. G. Peto

3445. Analytical chemistry of zirconium. I. Solochrome violet R as indicator for the micro- and macro-titration of zirconium with EDTA. J. Korkisch and A. Farag (II Chem. Inst., Vienna Univ., Austria). *Z. anal. Chem.*, 1959, **165** (1), 6–10.—Solochrome violet R (C. I. Mordant Violet 5) forms a red - violet complex with Zr in hot *N* HCl and is useful as an indicator for the titration of Zr with EDTA. The accuracy for 1·0 to 10 mg and 10 to 50 mg of Zr in 25 ml is within $\pm 1{\cdot}0$ and $\pm 0{\cdot}2\%$, respectively, and for 10 to 1000 μg of Zr in 10 ml, by micro-titration, within $\pm 1{\cdot}0$ μg. Large amounts of Sn^{2+}, Fe^{3+} or V^{5+} affect the indicator, and coloured ions (Cu, Cr^{3+}, Co and Ni) affect the end-point; Mo, W and Ti^{4+} form complexes with the indicator and interfere, as do PO_4^{3-} and F^-. Interference by F^- is eliminated by the addition of 2·5% $ThCl_4$ soln. in *N* HCl. *Procedure*—Adjust the soln. of Zr with HCl until it is 1 *N* and heat in boiling water (1 to 2 min.). In the presence of Fe^{3+} add 0·1% $SnCl_2$ soln. dropwise until the Fe is completely reduced. Add a 0·1% soln. of indicator (0·5 ml per 10 ml) and heat for 1 min. Titrate with EDTA soln. (disodium salt) to the orange end-point and correct the result by a blank.

J. P. Stern

3446. Rapid determination of zirconium in ferro-zirconium by EDTA titration. Shigeo Wakamatsu (Toto Seiko Co., Minami-sunamachi, Koto-ku, Tokyo). *Japan Analyst*, 1958, **7** (9), 578–581.—For the back-titration of the excess of EDTA with Cu^{2+} in the presence of Zr (and Hf), 1-(2-pyridylazo)-2-naphthol (**I**) (at pH 3) is the best indicator. Interfering ions, including Fe^{3+}, Ni and Cu, are extracted with cupferron (**II**) in diethyl ether from an aq. soln. containing EDTA (pH 1·5). The time taken for a determination is $\simeq$30 min. *Procedure*—Decompose the sample (200 mesh, 0·5 g) with HCl (50 ml) and NH_4F (2 g) and oxidise the Fe with HNO_3 (2 ml). Heat with $HClO_4$ (20 ml) until white fumes appear. Dissolve in water (50 ml); fuse the residue, if any, with Na_2CO_3, dissolve the melt in HCl (1:4, a few ml), add it to the soln. and make up to 250 ml. Dilute a 25-ml portion together with EDTA (0·0125 *M*, 30 ml) to 100 ml. Adjust the pH to 1·5 with ammonium acetate soln. (50%), add **II** (5%, 10 ml) and extract with ether (80 ml) for 1 min. Transfer the aq. layer into acetone (20 ml), adjust the pH to 3·0, add **I** (0·1% in methanol, 1 or 2 drops) and titrate with $CuSO_4$ soln. (0·0125 *M* in 0·35 *N* H_2SO_4) to a red colour.

K. Saito

3447. Gravimetric determination of zirconium in titanium. J. H. Hill and M. J. Miles (Titanium Metals Corp. of America, Henderson, Nev.). *Anal. Chem.*, 1959, **31** (2), 252–254.—Zirconium is pptd. from an HCl soln., containing from 0·15 to 0·2 g of Zr, by mandelic acid. After filtration, the Zr mandelate is dissolved in aq. NH_3 soln. and the soln. is filtered to remove any Ti associated with the first ppt. After re-pptn., the Zr mandelate is ignited to ZrO_2 and weighed. Interference is caused by Hf and Nb, giving high results. No interference is caused by the presence, in the amounts usually found in titanium alloys, of Fe, Al, V, Sn, Cu, Cr, Co, Mg, Mn, Mo and Ni. The method is applicable to the determination of Zr in ores and residues, provided that SO_4^{2-} are removed when decomposition has been effected by means of $KHSO_4$ fusion; Zr and Ti are pptd. as hydroxides by aq. NH_3 soln. and SO_4^{2-} are removed in the filtrate. The ppt. is re-dissolved in HCl and the procedure carried out as for alloys.

F. L. Selfe

3448. Determination of hydrogen in zirconium hydride. W. H. Jones (Wright Air Devel. Center, Materials Lab., Wright-Patterson AFB, Ohio). *U. S. Atomic Energy Comm.*, Rep. WADC-TN-57-294, 1957, 9 pp.—The determination is based on the measurement of the equilibrium pressure of hydrogen over the metal in a closed system under predetermined conditions. The results of analysis of 35 samples at temp. ranging from 1900° to 1000° and collection times from 10 to 30 min. are reported.

Nucl. Sci. Abstr.

3449. Colorimetric determination of trace amounts of cobalt in zirconium and titanium with the aid of mercury cathode electrolysis. Atsushi Mizuike and Shizo Hirano (Inst. Techno-anal. Chem., Fac. of Engng, Tokyo Univ., Hongo). *Japan Analyst*, 1958, **7** (9), 545–548.—The electrolytic separation of <10 μg of Co, followed by distillation of mercury (*cf.* Schmidt and Bricker, *Anal. Abstr.*, 1956, **3**, 1328) was examined with ^{60}Co. By electrolysis for 3 hr. (7·5 V, 1·9 amp.), more than 98% of the Co is separated by mercury in *N* H_2SO_4 (100 ml) containing $Zr(SO_4)_2$ (≡ 1 g of Zr). Mercury is evaporated off in a current of N at 350°. Colorimetry is effected by Sandell's method. *Procedure*—Dissolve the sample (≡ 1 g of Zr) in H_2SO_4 (25 ml) and dilute to produce 100 ml of *N* H_2SO_4 soln. Dissolve titanium metal (1 g) in H_2SO_4 (5·1 ml) and H_2O and dilute to 100 ml. Electrolyse the soln. with 2 ml of mercury for 3 hr. with stirring (7·5 V, 2 amp.; 0·5 amp. per sq. cm at the cathode). Evaporate off the mercury, dissolve the residue in aqua regia (5 ml) and evaporate to dryness. Add water (2·5 ml) and citric acid (0·2 *M*, 1·0 ml), adjust the pH to 7·8 to 8·0 with phosphate buffer (1·2 ml), heat in a water bath with nitroso-R salt soln. (0·2%, 0·5 ml), cool in the dark, again heat with HNO_3 (1:1, 2·0 ml) for 4 min., cool and measure the extinction at 420 mμ.

K. Saito

3450. Quantitative spectrographic determination of hafnium in zirconium dioxide. E. I. Kibisov (State Inst. Appl. Chem., Leningrad). *Zhur. Anal. Khim.*, 1958, **13** (6), 653–656.—Two methods, one for low concn. (0·001 to 0·005%) and the other for average concn. (≃3%), have been developed for the quant. determination of Hf in zirconium dioxide. For low concn. of HfO_2, much of the background is eliminated by the use of a discontinuous exposure, and a completely new method of introducing the sample is described. A sample is prepared by mixing 50 mg of ignited and well-ground zirconium oxide for 4 min. in a mortar with 1 ml of glycerol. The hafnium line Hf I 2940·77 was observed at concn. of the order of 0·001 to 0·005%. As a reference line, Zr 2942·3 was used. To determine average concn. of HfO_2, spectrographs Q-24 and ISP-22 were used. One drop of the glycerol emulsion of the sample is introduced on to the cold carbon electrode, which is then placed on a hot-plate for 20 min. until all "smoking" ceases. A d.c. arc is used for exciting the spectrum. The gap used is 3·5 mm, the current strength is 6 amp, and the exposure time is 30 sec. As a base line Hf II 2641·4 and as a reference line Zr 2619·2 were used. The glycerol suspensions of the sample should not be stored for more than 12 hr.

W. Roubo

3451. Determination of small amounts of zirconium and hafnium in silicate rocks. A. M. Tuzova and A. M. Nemodruk (V.I. Vernadsky Inst. Geochem. and Anal. Chem., Acad. Sci., Moscow). *Zhur. Anal. Khim.*, 1958, **13** (6), 674–676.—A method is described for concentrating Zr and Hf from silicate rocks containing a total of both elements of $0·5 \times 10^{-4}$ to 1×10^{-4} %. The procedure involves the pptn. of the elements with phenylarsonic acid followed by re-pptn. by means of *p*-(*p*-dimethylaminophenylazo)benzenearsonic acid (**I**). Take 5 to 10 g of finely divided sample and decompose it in a platinum crucible by means of HCl and HF or H_2SO_4 and HF. After decomposition and removal of HF is complete, dissolve the residue in 50 ml of 2 *N* HCl and dilute with water to make the soln. *N* with respect to HCl. Add 1 to 2 ml of 30% H_2O_2 soln. (for complexing Ti), then introduce 5 to 6 ml of 20% phenylarsonic acid soln. to precipitate Zr and Hf and allow the ppt. to settle for 24 hr. Filter off and wash the ppt. with a 0·1% soln. of phenylarsonic acid in 0·1 *N* HCl, dry, then ignite for 1·5 to 2 hr. at 900° to 1000°. Fuse the dioxides of Zr and Hf thus obtained with $K_2S_2O_7$, dissolve the melt in 50 ml of 6 *N* HCl and warm on a water bath for 10 to 15 min. After cooling the product, add 1 to 2 ml of 30% H_2O_2 soln., 5 ml of a 2% soln. of the sodium salt of **I**, 30 to 35 ml of water and 10 ml of 1% methyl orange soln. After 24 hr. filter off the ppt., wash it 2 or 3 times with a 0·1% soln. of **I** in 0·1 *N* HCl, dry and ignite at 900° to 1000°. Each of the elements is determined in the concentrate thus obtained by X-ray spectral analysis. Since the recovery of the elements is very high (94 to 100%), the accuracy of the method is correspondingly high.

W. Roubo

3452. Determination of radiogenic helium in zircon by stable isotope dilution technique. P. E. Damon and J. L. Kulp (Lamont Geol. Observatory, Palisades, N.Y., U.S.A.). *Trans. Amer. Geophys. Union*, 1957, **38**, 945–953.—Zircon samples have been analysed for He by an isotopic dilution technique in which ^3He was used as a spike. The precision of this method is about ±3% and gives a He content 15% higher than that given by techniques used by previous investigators. Non-metamict zircon samples studied indicate that a retentivity of He of >80% is not unusual. Metamict zircons retained only 1% of radiogenic He.

Chem. Abstr.

3453. Analytical chemistry of hafnium. L. M. Komissarova and V. E. Plyushchev (M.V. Lomonosov State Univ., Moscow). *Zhur. Anal. Khim.*, 1958, **13** (6), 709–715.—A review, with 67 references. W. ROUBO

3454. Ultra-violet spectrophotometric determination of thorium with 2 : 4-dichlorophenoxyacetic acid. Sachindra Kumar Datta (Chem. Dept., Darjeeling Gov. Coll., India). *Anal. Chem.*, 1959, **31** (2), 195–197.—*Procedure*—Dilute the soln. (containing 2 to 20 mg of Th as nitrate) to 20 ml and adjust the pH to 2·4. Heat to 80° and precipitate Th by the addition of an excess of a hot 1% soln. of 2:4-dichlorophenoxyacetic acid. Set aside for 5 min. and filter through a No. 3 porosity glass filter-crucible. Wash successively with a 0·1% soln. of the reagent, hot ethanol and diethyl ether. Dissolve the ppt. in 0·08 *M* ammonium carbonate soln. (50 ml), and dilute to 1 litre. Measure the extinction at 230 mμ against a reference soln. containing the same concn. of ammonium carbonate. Bi- and ter-valent Fe, Ce^{4+} and Zr^{4+} interfere seriously, but only slight interference is caused by Ni, Co and U. Optimum results are obtained with 2 to 14 mg of Th. The accuracy is poor in samples containing <2 mg of Th. F. L. SELFE

3455. Amperometric titration of thorium in monazite. Shao-Chun Tung and Er-Kang Wang (Inst. of Appl. Chem., Acad. Sinica). *Acta Chim. Sinica*, 1959, **25** (1), 33–37.—The dried sample (3 g) is fused with KHF_2 (12 g) in a platinum crucible. The melt is treated with hot water (70 ml) and HF (20 ml). By employing a mixture of $AlCl_3$ (30 g), acetic acid (17·5 ml) and Na acetate (2 g) in 250 ml as supporting electrolyte, Th is determined by amperometric titration at 25° with standard ammonium molybdate soln. at an applied potential of −0·75 V *vs.* the S.C.E. The error of the method is $<\pm 2\%$. A complete analysis takes 3 hr. S. H. YUEN

3456. Spectrographic determination of scandium, yttrium and the rare earths in thorium. J. P. Faris (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Appl. Spectroscopy*, 1958, **12** (6), 157–161.—The thorium is dissolved in 8 *N* HNO_3 and passed through a column of Dowex-1 anion resin. The impurities in the eluate are then determined by the copper-spark technique with an accuracy of about $\pm 40\%$ when the spectra are visually compared with standard spectra and of about $\pm 5\%$ when a densitometric procedure is used to evaluate the spectra. K. A. PROCTOR

3457. Conductimetric method for the estimation of small quantities of ammonia. J. Shaw and B. W. Staddon (King's Coll., Newcastle upon Tyne, England). *J. Exp. Biol.*, 1958, **35** (1), 85–95.—Ammonia is liberated from the sample by alkali (3 to 5 μl of half-satd. KBO_2 soln.) and absorbed in a small drop of standard acid soln. (1 to 3 μl of H_2SO_4, *e.g.*, 0·001 *N*) by Conway's diffusion method. At the end of the diffusion period the acid drop is transferred to a small conductivity cell maintained at constant temp., and made up to the mark with H_2O. The conductance of the soln. is measured and the percentage of the acid neutralised is calculated by reference to a calibration curve. The electrical conductance of the acid falls as NH_3 is absorbed, owing to the difference in the mobility of H^+ and NH_4^+. Results for standard $(NH_4)_2SO_4$ soln. and biological fluids are tabulated. The method can be applied to amounts down to 0·005 μg of ammonia-N with a standard deviation of $<\pm 2\%$; with 0·001 μg of ammonia-N the error is $\pm 8\%$. The construction of small diffusion chambers and small conductivity cells is described. K. R. C.

3458. Analysis for industry. A. M. G. Macdonald. *Ind. Chemist*, 1959, **35** (1), 88–91.—A review is given of the use of organic base molybdophosphates in the determination of phosphorus. O. M. WHITTON

3459. Critical factors in the turbidimetric microdetermination of phosphorus as strychnine molybdophosphate. A. J. Hegedüs and M. Dvorszky (Forschungsinst. f. d. nachrichtentech. Ind., Tungsram, Budapest). *Mikrochim. Acta*, 1959, (1), 141–159.—The determination of traces of P as strychnine molybdophosphate has been studied to ascertain the effect of the several variables on the determination. The following procedure illustrates optimum conditions. Transfer the soln. (>25 μg of P) to a 25-ml flask, add 3·7 ml of 8 *N* HNO_3 and 2·5 ml of strychnine - molybdic acid soln. (0·2 *M* in MoO_3, 4 *M* in HNO_3, 0·173 *M* in $NaNO_3$ and 0·004 *M* in strychnine nitrate). Dilute the soln. to 25 ml, mix and set aside for 1 hr. at 20° before recording the extinction at 720 mμ. Results (20) at a level of 12 μg of P were all within ±0·3 μg of P. T. R. ANDREW

3460. Determination of phosphorus in low-grade uranium ores. E. Booth [U.K.A.E.A. (Res. Group), Woolwich Outstation, C37, Royal Aresenal, Woolwich, London]. AERE-AM 7, 1959, 3 pp.—The ore, after sintering at 450° with Na_2O_2, is dissolved in dil. HNO_3 and the P is determined absorptiometrically in a suitable aliquot as the molybdovanadophosphate complex. The method is applicable to ores containing up to 0·5% of P and the coeff. of variation at the 100 p.p.m. level is $\simeq \pm 2\%$. (*Cf.* Elwell and Wilson, *Analyst*, 1956, **81**, 136.) N. E.

3461. Use of radioactive phosphorus in the study of phosphate separations. P. H. Bailey and R. W. C. Broadbank (Sch. of Chem., Coll. of Technol. and Commerce, Leicester, England). *Analyst*, 1958, **83**, 675–679.—Phosphate ions labelled with ^{32}P have been used to study the efficiencies of the basic acetate, the metallic tin and the zirconium nitrate procedures for the removal of PO_4^{3-} in semi-micro qual. analysis. The ^{32}P (0·05 to 0·1 μC) was added to standard soln. of calcium phosphate or KH_2PO_4. In each method the activity of the ppt. and of the supernatant liquid was determined, with the necessary corrections for background activity and lost counts, and the percentage of PO_4^{3-} recovered from the soln. was calculated. Small amounts of PO_4^{3-} are efficiently removed from soln. by both the basic acetate and the metallic tin procedures. The procedure with $Zr(NO_3)_4$ is satisfactory provided that an excess of reagent is avoided, especially with small amounts (*e.g.*, 3 to 5 mg) of PO_4^{3-}, the optimum ratio being three Zr atoms to two PO_4^{3-} ions. A. O. JONES

3462. Method for determination of oxygen-18 content of inorganic phosphate. F. R. Williams and L. P. Hager (Converse Mem. Lab., Harvard Univ., Cambridge, Mass., U.S.A.). *Science*, 1958, **128**, 1434.—In the method described, the phosphate is heated in an evacuated tube with $Hg(CN)_2$ at 250°

for 1 hr. The CO_2 formed is collected and introduced into the mass spectrometer for measurement of ^{18}O. H. F. W. KIRKPATRICK

3463. **Analysis of commercial sodium tripolyphosphate by reverse-flow ion-exchange chromatography.** R. H. Kolloff (Monsanto Chemical Co., St. Louis, Mo., U.S.A.). *Bull. A.S.T.M.*, 1959, (237), 74–80.—Apparatus and procedure are described whereby a complete and accurate analysis of commercial $Na_5P_3O_{10}$ can be made in <90 min. A soln. of the sample ($\simeq 20$ mg), together with aq. *M* KCl (pH 5), is passed through a column (37 cm by 2 cm) of Dowex 1X-10 (200 to 400 mesh, Cl form) by the pressurised continuous-gradient "upflow" elution technique (Grande and Beukenkamp, *Anal. Chem.*, 1956, **28**, 1497; Schwab *et al.*, *Ibid.*, 1957, **29**, 1357). The total pressure applied to the column is $\simeq 200$ cm of water for a flow-rate of $\simeq 6$ ml per min. The order of elution of the fractions is—ortho-, pyro-, tri-, tetrameta- and trimeta-phosphate; long-chain phosphates are retained on the column and can be determined by difference. A quant. determination of the phosphate in each fraction (one only for each compound) is made by an improved and standardised spectrophotometric procedure based on the molybdenum blue method. The reverse-flow elution and the finer resin particles ensure a sharper separation of the phosphate species. The method is more accurate and rapid than the ion-exchange procedure given previously (*cf.* Spangler *et al.*, *Anal. Abstr.*, 1959, **6**, 516). W. J. BAKER

3464. **Colorimetric determination of arsenic in lead - arsenic alloys.** Takashi Miura and Masao Ozeki (Matsushita Electric Ind., Chigasaki, Kanagawa-ken). *Japan Analyst*, 1958, **7** (11), 718–720.—Experimental conditions for the rapid (3 hr.) colorimetric determination of As in lead alloy (containing 2 to 10% of As) were examined. The molybdenum blue method is useful for $<0{\cdot}6$ mg of As per 100 ml; the influence of segregation in the alloy is eliminated by taking a large amount of sample. *Procedure*—Dissolve the sample (4 g) in HNO_3 (1:3, 30 ml) and H_2O_2 (30%, 10 ml), then heat with H_2SO_4 (1:1, 10 ml), cool, and make up to 1 litre (without filtration). Make a 10-ml aliquot alkaline with 3 *N* NaOH, boil to expel H_2O_2, make acid with H_2SO_4 (1:10) and dilute to 500 ml. Acidify a 50-ml aliquot with HNO_3 (1:1, 2 ml), neutralise with 3 *N* NaOH and make up to 100 ml after addition of H_2SO_4 (1:10, 10 ml), $(NH_4)_2MoO_4$ soln. (2%, 4 ml) and hydrazine sulphate soln. (1%, 15 ml). Immerse in boiling water for 15 min., cool, and measure the extinction at 750 mμ. K. SAITO

3465. **Precise micro-heterometric determination of bismuth as iodide with Pyramidon [amidopyrine]. A study of the reaction and of the compounds.** M. Bobtelsky and M. M. Cohen (Hebrew Univ., Jerusalem). *Anal. Chim. Acta*, 1959, **20** (1), 1–15.—Volumetric methods are described for the determination of Bi and amidopyrine (**I**) by the heterometric titration procedure (Bobtelsky, *Anal. Chim. Acta*, 1955, **13**, 172). Bismuth ($\simeq 1$ mg) in $0{\cdot}1\ M$ HNO_3 containing KI is titrated with $0{\cdot}00125\ M$ **I**. In the reverse procedure, **I** is titrated with $0{\cdot}005\ M$ $Bi(NO_3)_3$. The method is rapid and accurate and is unaffected by the presence of alkaline-earth and heavy metals up to 80 to 90% of the total metal content. W. T. CARTER

3466. **Complexometric titrations (chelatometry). XLI. Photometric titrations of bismuth and copper using catechol violet as indicator.** V. Suk and V. Miketuková (Inst. Anal. Chem., Charles' Univ., Prague). *Chem. Listy*, 1958, **52** (12), 2408–2409.—*Procedure for Bi*—Dilute the soln. of $Bi(NO_3)_3$ in the photometric titration cell to 70 to 100 ml, add catechol violet soln. (**I**) (0·1%) (3 to 4 drops) as indicator, adjust the pH to 2 to 3 with aq. NH_3 till blue, and titrate photometrically with $0{\cdot}01\ M$ EDTA (disodium salt) (**II**) till yellow, with the use of a yellow filter; 0·2 to 140 mg of Bi can be determined with an accuracy of $\pm 0{\cdot}11\%$. Interference by Fe^{3+} can be avoided by the addition of ascorbic acid. *Procedure for Cu*—Dilute the soln. of Cu^{2+} to 70 to 100 ml with water, add NH_4NO_3 soln. (10%) (5 ml), 4 to 5 drops of **I** and aq. NH_3 dropwise till blue. Add Na acetate soln. (20%) (5 ml) and titrate with **II** till green, with the use of a yellow filter; 1 to 35 mg of Cu can be determined with an accuracy within $\pm 0{\cdot}08\%$. The titrations were carried out with the use of a Lange photometer and the end-point was determined graphically. J. ZÝKA

3467. **Effect of pre-saturation of the paper on the sequence of bismuth - cadmium in paper chromatography with butanol - normal hydrochloric acid.** J. A. Coch-Frugoni (Lab. Curie, Inst. du Radium, Paris). *J. Chromatography*, 1959, **2** (1), 69–71.—When a mixture containing Bi and Cd is chromatographed with this solvent system without previous saturation of the paper, Cd precedes Bi, but when the paper is brought into equilibrium by exposure to the solvent vapour for 24 hr. the order is reversed. Pre-saturation does not improve the separation, but the effect is important in the measurement of R_F values. G. BURGER

3468. **Spectrophotometric determination of vanadium by extraction of tungstovanadophosphoric acid with ethyl methyl ketone.** Hiroshi Kitagawa and Norio Shibata (Hitachi Central Res. Lab., Kokubunji, Tokyo). *Japan Analyst*, 1958, **7** (10), 624–627.—Tungstovanadophosphoric acid is extracted from $0{\cdot}5\ N$ H_2SO_4 soln. with ethyl methyl ketone (**I**). The extinction at 440 mμ is proportional to the concn. of V for $<0{\cdot}8$ mg per 25 ml of **I**. There is no interference from coloured ions, including Fe^{3+} (<5 mg), Ni, Co, Mn and Cu (<200 mg each). Chromium is removed as chromyl chloride. *Procedure*—Heat the sample soln. to white fumes with H_2SO_4 (1:1, 3 ml), dissolve in HCl (1:1, 10 ml) and water (20 ml), neutralise with NaOH soln. (6 *N*) and make up to 50 ml after the addition of H_2SO_4 (5 *N*, 5 ml) and H_3PO_4 (1:2, 1 ml). Heat the product to 100°, add Na_2WO_4 soln. ($0{\cdot}5\ M$, 0·5 ml), then cool and extract with **I** saturated with $0{\cdot}5\ N$ H_2SO_4. K. SAITO

3469. **Determination of vanadium and chromium by photometric titration.** V. F. Barkovskiĭ (Ural State Inst. A.M. Gorky, USSR). *Zhur. Anal. Khim.*, 1958, **13** (6), 682–685.—*Determination of V in ferrovanadium*—Dissolve the ferrovanadium (0·05 g) by heating in H_2SO_4 (1:3) (5 ml), add HNO_3 (1:1) (1 ml) and heat for 1 to 2 min., cool, make up to 60 to 70 ml with H_2O, add $KMnO_4$ soln. dropwise until a stable pink colour is obtained; decompose the excess of $KMnO_4$ with satd. oxalic acid soln. and titrate photometrically with $0{\cdot}02\ N$ $(NH_4)_2SO_4.FeSO_4$. *Determination of V in steel containing no W*—To the sample (1 to 3 g) add H_2O (30 ml) and 25 ml of an acid mixture (15 ml of

H_2SO_4, sp. gr. 1·84, and 10 ml of H_3PO_4, sp. gr. 1·7); dissolve by heating, decomposing the carbides by the addition of conc. HNO_3 (0·5 ml), and continue as described above. *Determination of V in steel as a phosphorus - tungsten - vanadium complex*—Dissolve the steel (0·2 to 1·0 g) by heating with 15 to 20 ml of an acid mixture (H_2O, H_2SO_4, sp. gr. 1·84, and H_3PO_4, sp. gr. 1·7) (1:1:1), decompose the carbides with HNO_3, cool, make up to 60 to 70 ml with H_2O, and if W is absent from the steel add 0·05 *N* sodium tungstate (5 ml); add $KMnO_4$ soln. and continue as described above. *Determination of V and Cr in a single steel sample*—Dissolve the sample (0·5 g) by heating in 30 ml of an acid mixture (380 ml of H_2O, 90 ml of H_2SO_4, sp. gr. 1·84, and 60 ml of H_3PO_4, sp. gr. 1·7), decompose the carbides by the dropwise addition of HNO_3, evaporate the soln. until H_2SO_4 fumes appear, add hot H_2O, and if W is absent from the steel add 0·05 *N* sodium tungstate; add 0·5% $CoSO_4.7H_2O$ soln. (10 ml) and heat to boiling; add freshly prepared 25% $(NH_4)_2S_2O_8$ soln. (20 ml) to the boiling soln. and continue boiling for a further 1 to 2 min. until a crimson permanganate colour appears. Place the soln. on a hot-plate until the $(NH_4)_2S_2O_8$ is completely decomposed and then boil again; add 5% NaCl soln. (10 ml) and continue heating for 5 to 10 min. after the permanganate colour is discharged. Titrate the cool soln. with 0·05 *N* $(NH_4)_2SO_4.FeSO_4$. The absolute error did not exceed 0·05% and the relative error was between +0·01 and −0·09%, according to the sample used.

K. R. C.

3470. **Separation of vanadium, molybdenum and tungsten by paper chromatography. I.** Shih-fu Tzou and Shu-chuan Liang. *Acta Chim. Sinica*, 1958, **24** (5), 383–387.—The method of Pollard has the disadvantages that (*i*) tailing takes place with V and Mo and (*ii*) W remains at the origin, which tends to retain some Mo. By keeping the valency and the state of association unchanged during elution and by forming stable and soluble complexes of the elements to be tested, these faults can be avoided. The per-acids formed by V, Mo and W with H_2O_2 were found to be satisfactory. Seven eluents were tested, Nos. 1, 2 and 3 comprising *n*-butanol - H_2O_2 - HNO_3 in slightly different ratios; the R_F values are almost the same. Eluents 4 and 5 comprise the first three solvents containing dioxan and benzoylacetone, respectively. The R_F values for V, Mo and W with eluents 4 and 5 are several times as great as those with eluents 1 and 2. In eluents 6 and 7, $(NH_4)_2S_2O_8$ is used instead of H_2O_2; the results are not promising as the spots of V and W diffuse to a pronounced degree and the spot of W moves very little ($R_F = 0·01$). A table of R_F values is given for the three elements when chromatographed singly and in admixture, and diagrams of typical chromatograms are given. The separation of V^V, Mo^{VI} and W^{VI} from one another is possible with eluents 1 to 3. With eluents 4 and 5 it is possible to separate V from Mo, Mo from W, and Mo from both V and W, but it is impossible to separate V and W. With eluents 6 and 7 it is possible only to separate Mo from V and V from Mo.

Sci. Abstr. China

3471. **Total assay of high-purity niobium metal by differential spectrophotometry.** R. O. Backer, V. R. Wiederkehr and G. W. Goward (Westinghouse Electric Corp., Bettis Plant, Pittsburgh). *U.S. Atomic Energy Comm.*, Rep. WAPD-204, 1958, 10 pp.—Samples are dissolved in HF and HNO_3 and fumed with H_2SO_4. Niobium is determined by differential spectrometric measurement of the peroxyniobate complex formed in a mixture of H_3PO_4 and H_2SO_4. The method covers a concn. range of from 92·3 to 100·0% of niobium. The relative standard deviation of the method is approx. ±0·1%.

Nucl. Sci. Abstr.

3472. **Colorimetric determination of tantalum in presence of niobium.** G. Popa, D. Negoiu and G. Baiulescu (Fac. of Chem., "C. I. Parhon" Univ., Bucharest, Romania). *Z. anal. Chem.*, 1959, **165** (1), 16–19.—The colour reactions of Ta and Nb with three flavone derivatives are examined; Ta forms coloured complexes with quercetin (**I**) and with 3-hydroxy-5:7:3′:4′-tetramethoxyflavone, but not with 5-hydroxy-3:7:3′:4′-tetramethoxyflavone; Nb reacts with none of the three reagents. Thus Ta can be determined in the presence of Nb. The Ta soln. (prepared from Ta_2O_5 by fusion with $KHSO_4$ and dissolution of the melt in 3% ammonium oxalate) is treated with a soln. of **I** [0·1% in ethanol - conc. HCl (3:1)] (5 ml) and diluted to 10 ml with ethanol; the extinction is then measured in a Pulfrich photometer (1-cm cell) with a M47 filter; 5 to 80 μg of Ta in 10 ml can be determined in the presence of a fivefold excess of Nb.

J. P. Stern

3473. **Extraction of sulphur-35 from pile-irradiated potassium chloride.** R. G. Deshpande (Atomic Energy Estab., Trombay, Bombay, India). *J. Chromatography*, 1959, **2** (1), 117–118.—Carrier-free ^{35}S produced by irradiation of KCl can be separated from K^+ and ^{32}P by means of a column of Amberlite IRA-400 resin in the Cl^- form. The aq. soln. is passed down the column which is then washed with water. The percolate and water contain some ^{32}P. The column is then eluted with 0·1 *M* HCl and the eluate collected in 50-ml fractions. The first few fractions contain ^{32}P free from ^{35}S, and the later fractions contain pure ^{35}S, giving complete separation.

G. Burger

3474. **Collection and turbidimetric estimation of sulphur trioxide in flue gases.** D. H. Napier and M. H. Stone (Brit. Coal Utilisation Res. Ass., Leatherhead, Surrey). *J. Appl. Chem.*, 1958, **8** (12), 787–793.—The improved turbidimetric procedure described enables SO_3 in the concn. range 6 to 80 mg per litre to be determined with a precision of ±2% and with a lower precision in the range 1 to 6 mg per litre. The improvements include temp. control during pptn., the addition of solid $BaCl_2$ of standard purity, and the control of the aq. *iso*propyl alcohol soln., the concn. of which is kept at 39·5% by wt. An improved sampling apparatus is also described, together with modifications to a commercially available turbidimeter.

J. H. Waton

3475. **Paper-chromatographic separation of several inorganic anions containing sulphur and their identification by infra-red spectrography.** Y. Garnier and C. Duval (École Nat. du Chim., Paris). *J. Chromatography*, 1959, **2** (1), 72–75 (in French).—The chromatographic behaviour of SO_4^{2-}, HSO_4^-, $S_2O_7^{2-}$, $S_2O_6^{2-}$, $S_4O_6^{2-}$ and $S_5O_6^{2-}$ has been studied with the solvent systems *n*-butanol - H_2O and *iso*propyl alcohol - H_2O. The chromatograms were developed with ethanolic benzidine and $KMnO_4$, the bands cut out and the anions dissolved in H_2O for spectrographic determination. The method is suitable for the determination of microgram quantities; R_F values are recorded.

G. Burger

3476. **Colour reaction for sulphate ion.** H. Weisz (Inst. f. anorg. u. allg. Chem., Tech. Hochsch., Vienna). *Mikrochim. Acta*, 1959, (1), 26–28.—Sulphate ion (0·5 μg) can be detected by spotting the test soln., weakly acid with acetic acid, on a paper that has been treated successively with drops of 0·1% $Ba(NO_3)_2$ soln., 1% Na rhodizonate soln. and 0·5% $AgNO_3$ soln. The intense violet colour of Ag rhodizonate makes the test more sensitive than the simple liberation of rhodizonic acid. Interference by halides and sulphides is overcome by adding excess of $AgNO_3$ to the test drop. Chromate and phosphate do not interfere.
T. R. ANDREW

3477. **Analysis of mixtures of sulphuric acid with other acids by non-aqueous titration.** Mihir Nath Das and Debabrata Mukherjee (Jadavpur Univ., Calcutta, India). *Anal. Chem.*, 1959, **31** (2), 233–237.—Procedures are given, and discussed, for the potentiometric titration of H_2SO_4 as a mono- or di-basic acid with 0·1 *N* NaOH in ethanediol - acetone (2:1). Provided that weak acids are absent, 0·1 *N* piperidine is preferred to NaOH as titrant in glycolic media. The method is applicable quant. to binary mixtures of H_2SO_4 with HNO_3, HCl, $HClO_4$, H_3PO_4, acetic acid, salicylic acid or toluene-*p*-sulphonic acid and also, but with much less accuracy, to ternary mixtures containing, in addition to H_2SO_4, a weak acid and a strong or moderately strong acid (*e.g.*, a mixture of H_2SO_4, H_3PO_4 and salicylic acid). When H_3PO_4 is present, the titration is preferably made with NaOH or piperidine in ethanediol - *iso*propyl alcohol (2:1). The conductimetric titration of H_2SO_4 with piperidine in glycolic media also gives two inflections in the titration curve.
W. J. BAKER

3478. **Analysis of sulphonyl chlorides by "polarovoltric" titration with sodium sulphide.** M. R. F. Ashworth, W. Walisch and G. Kronz-Dienhart (Inst. for Org. Chem., Univ. of the Saar, Saarbrücken, Germany). *Anal. Chim. Acta*, 1959, **20** (1), 96–98.—Sulphonyl chlorides in 50% aq. acetone can be titrated with standard Na_2S soln. In the range 0·05 to 0·1 *M* a colour change indicates the end-point, but if a "polarovoltric" apparatus is used with polarised platinum electrodes, potentiometric titrations can be carried out with soln. as dilute as 0·005 *M*.
W. T. CARTER

3479. **Application of thio salts in analysis. II. Estimations based on the decomposition of thio salts. Part F. Estimation of selenium and tellurium in selenites and tellurites.** G. B. S. Salaria (Chem. Dept., Gov. Coll., Rohtak, Punjab, India). *Anal. Chim. Acta*, 1958, **19** (6), 604–605.—Quadrivalent Te and Se^{IV} may be pptd. as sulphides in readily collected form by addition of Na_2S soln. (2 *N*) and subsequent acidification of the soln. with HCl to 6 *N* followed by heating almost to boiling-point.
T. R. ANDREW

3480. **Micro-determination of chromium in collagen sutures.** E. R. Hoffmann and M. G. Comfort (Ethicon Inc., Somerville, N.J., U.S.A.). *Microchem. J.*, 1958, **2** (2), 263–275.—The sutures (3 to 10 mg of dried material) are mineralised by fusion with potassium peroxydisulphate (400 to 800 mg) in a platinum or quartz crucible. After dissolution of the melt, the Cr is oxidised to the sexavalent state with hypobromite. Excess of oxidant is removed and the Cr is caused to react with a large excess of *sym.*-diphenylcarbazide soln. at pH 1·1, and the extinction is measured at 542 mμ. The standard deviation on 3 to 12-mg samples containing 0·4 to 0·8% of Cr_2O_3 is ±0·006. A single determination, including weighing of sample, is completed in < 15 min.
D. F. PHILLIPS

3481. **Rapid determination of the chromate ion by means of a detector tube.** Yoshitaka Kobayashi (Fac. of Engng, Yokohama Univ., Minami-ku). *Japan Analyst*, 1958, **7** (9), 560–564.—Silica gel (60 to 80 mesh) is impregnated with Pb acetate (0·4 mg per 1 g of the gel) and placed in a glass tube (diam. 2 mm, length of the silica gel column, 60 to 80 mm). When the column is percolated with the sample soln. (>2 p.p.m. of CrO_4^{2-}), a yellow layer is produced, the length depending on the concn. of the CrO_4^{2-}. The influence of grain size, water content of the gel and diameter was examined. The length of the coloured layer is independent of the pH in the range 2·0 to 8·0 and of the temp. (15° to 60°). The coloration is complete within 3 min. and remains unchanged for >10 min. The error is <10%.
K. SAITO

3482. **Iron analysis in chromium solutions.** A. Salka. *Metal Finish.*, 1958, **56** (12), 64.—The upper limit of Fe permissible in the chromium-plating bath is ≃15 to 20 g per litre. Iron is separated as $FePO_4$ and determined by complexometric titration with EDTA and ferron as indicator. The EDTA - Fe complex (**I**) shows a greater stability than the ferron - Fe one and, when all Fe has been changed into **I**, the end-point is marked by a sudden change in colour from green to yellow. The reagent is specific, but Cr^{3+} interfere and should be oxidised by $(NH_4)_2S_2O_8$.
S.C.I. ABSTR.

3483. **Determination of small quantities of molybdenum in tungstates.** C. Winterstein. *Z. Erzbergb. Metallhüttenw.*, 1957, **10**, 549–551.—Dilute the alkaline soln., obtained by fusion of the specimen and extraction with water, to a known vol. (MoO_3 content >0·01 g per ml). Treat the soln. (50 ml) with 30 ml of NaF soln. (20 g of NaF, 400 to 450 ml of H_2O and a few ml of 20% NaOH soln., heat, filter and dilute to 500 ml) and neutralise with H_2SO_4 (1:1), then add H_2SO_4 (1:1) (10 ml) in excess and stir to liberate CO_2. Cool to 12° to 15° and place in a separating-funnel. Add 10% KSCN soln. (10 ml), 3 ml of $SnCl_2$ soln. [10 g of $SnCl_2.2H_2O$ is dissolved in 30 ml of HCl (sp. gr. = 1·19) and diluted to 100 ml] and finally 85% butyl acetate (20 ml). Shake for 30 to 40 sec. and pass the lower layer into the original beaker. Repeat the shaking in the separating-funnel twice. The extraction is complete when the butyl acetate layer is colourless. Finally dilute the extract to 50 ml with butyl acetate and measure the colour with a Hg 436 filter. The extinction max. is at 470 mμ.
CHEM. ABSTR.

3484. **The use of metal-specific indicators in precipitation titrations. III. Determination of tungsten and molybdenum in synthetic samples.** E. Lassner, R. Scharf and R. Püschel (Metallwerk Plansee A.-G., Reutte/Tirol, Austria). *Z. anal. Chem.*, 1959, **165** (1), 29–32.—The method previously described (*cf.* Püschel *et al.*, *Anal. Abstr.*, 1959, **6**, 1719, 2126) is suitable for the rapid (30 min.) routine determination of W as tungstate in metal samples containing Cu, Ni, Fe and Th and in mixed carbides of W, Ti and Ta, and of Mo as molybdate in molybdenum concentrates. In

samples containing both W and Mo, simple titration gives the sum of the metals; in an aliquot, Mo is then separated by H_2S (W being masked by tartrate) and gravimetrically determined. For tungsten samples containing 80 to 98% of W, the average error is ±0·25%, and for molybdenum concentrates (60% of Mo) it is ±0·3%. Results agree with gravimetric results. *Procedure*—(*a*) Dissolve the tungsten sample (10 g) in HF - HNO_3, evaporate to dryness, and fuse the residue with $NaKCO_3$. Dissolve the melt in water, dilute to 1 litre, filter, and use 10 ml. (*b*) Fuse the molybdenum sample (2·5 g) with Na_2O_2 and dissolve the melt in water; add Na_2O_2 (1 g) and boil. Dilute the cold soln. to 1 litre, filter, and use 10 ml. Dilute the 10-ml aliquot from (*a*) or (*b*) to 250 ml, adjust to pH 2 to 3 with dil. HNO_3, and boil for some minutes. Add hexamine (1 g) and 0·1% aq. 4-(2-pyridylazo)resorcinol soln. (8 to 10 drops), as indicator, and titrate the boiling soln. with 0·1 *M* $Pb(NO_3)_2$ (added dropwise with stirring) to a persistent red colour. J. P. STERN

3485. **Determination of uranium by cupferron with Complexone III as the masking agent.** A. K. Majumdar and J. B. Ray Chowdhury (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1958, **19** (6), 576–577.—By pptn. with cupferron at pH 6 to 7 in a soln. containing a ten-fold excess of EDTA (disodium salt), U can be separated from Bi, Cu, Fe, Cr, Al, Th, Cd, Pb, Zn, Mn, Ni, Co, rare-earth metals, VO_3^-, MoO_4^{2-} and WO_4^{2-}; Ti, Be, Sn, Sb, As and PO_4^{3-} interfere. T. R. ANDREW

3486. **An extraction, controlled-potential coulometric method specific for uranium(VI).** G. L. Booman and W. B. Holbrook (Atomic Energy Div., Phillips Petroleum Co., Idaho Falls, U.S.A.). *Anal. Chem.*, 1959, **31** (1), 10–16.—*Cf. Anal. Abstr.*, 1959, **7**, 905.

3487. **New method based on paper chromatography for the determination of uranium in uranium minerals.** I. I. M. Elbeih and M. A. Abou-Elnaga (Dept. of Chem., Univ. of Cairo, Giza, Egypt). *Chemist Analyst*, 1958, **47** (4), 92–93.—The mineral (0·5 g for rich ores, up to 5 or 10 g for poor ones) is dissolved in a mixture of 10 ml of conc. HNO_3 and 1 to 2 ml of conc. HF with the aid of heat, and taken almost to dryness. The SiO_2 residue is extracted with 3 ml of conc. HNO_3 and 20 ml of hot water, filtered off and dried. The dissolution and extraction steps are repeated, and the united filtrates and washings made up to 100 ml. For rich ores, 0·01-ml spots are chromatographed as previously described for the visual comparison procedure (*Anal. Abstr.*, 1959, **6**, 855), the uranium spots being located on indicator strips with $K_4Fe(CN)_6$, and appropriate portions of the main paper, together with blanks, cut off and transferred to separate flasks. EDTA titration is carried out by the method of Kinnunen and Wennerstrand (*Chemist Analyst*, 1957, **46**, 92). The paper carrying a spot is shredded, treated with glacial acetic acid (1 ml), water (15 ml) and 0·001 *M* EDTA soln. (disodium salt) (5 ml), and boiled gently for 10 min. Ascorbic acid (0·2 g) is added, the mixture boiled gently for 10 min., cooled to 30°, and the excess of EDTA back-titrated with 0·001 *M* $Th(NO_3)_4$ soln., with xylenol orange as indicator. The mean of four such titrations is obtained, and corrected by the mean of four similar titrations carried out on blank spots. For poor ores, ten spots each of 0·01 ml of soln. are chromatographed as before on a wide paper, the appropriate zones of the test and blank papers being cut out and treated as described above. Tervalent Bi, Th^{3+}, Sn^{3+} and Sn^{4+} are not separated by the chromatographic procedure, and interfere with the EDTA titration, but not with the visual comparison procedure. Results for known amounts of U from 20 to 100 μg showed errors of from −1·5 to +1·2 μg. Six analyses of an Egyptian phosphate rock, using ten zones for each titration, showed recoveries from 0·009 to 0·011% of U (mean, 0·010%), the result by a standard method being 0·01%. R. E. ESSERY

3488. **Radiometric determination of uranium in ores.** L. G. Evans and C. Rampacek (U.S. Bur. of Mines, Tucson, Arizona). *U.S. Bur. Mines, Rep. Invest.*, 1958, (5390), 15 pp.—Rapid determinations were investigated and the two most promising ones were developed, namely the ratio and equilibrium methods. The ratio method consists in determining the radioactivity of the unknown sample by a Geiger counter and standard scaler counting unit under three different conditions. An open radioactive count is first made on the material, followed by the determination of the radioactivity through an aluminium filter and then through a lead filter. The open counting procedure records both the weak and the strong β-rays and about 5% of the γ-rays, while the aluminium filter passes only the strongest β-radiations and γ-rays; the lead filter removes substantially all the β-radiations and allows only the γ-rays to pass. By comparing the ratios of the open count to the counts obtained through the aluminium and lead filters it is possible to predict whether or not a sample is in or near radioactive equilibrium and whether the radioactivity is due to the presence of Th. The equilibrium method depends on the simultaneous measurement of the β- and γ-radiations given off by an ore. The apparent equiv. uranium content of the sample is then determined by comparing its β-activity with that of known assayed pitchblende standards in radioactive equilibrium. In a similar way the apparent equiv. uranium content of the sample is determined from the γ-activity. The true uranium content of the ore is then calculated from these two values. The radiometric results obtained from 100 random samples in various stages of equilibrium by the ratio method and by a modified equilibrium method are discussed. The samples contained 0·01 to 3·64% of U_3O_8 as determined by chemical analysis. The over-all accuracy of the equilibrium method was 28·1%. By comparison, the over-all error between the chemical analyses and the β-equiv. uranium values of the ratio method was about 200%. However, the error was only 16·2% for samples shown to be in equilibrium by the ratio method. The two methods are useful for distinguishing between ores that are in or out of radioactive equilibrium. Neither the ratio method nor the equilibrium procedure is a substitute for quant. chemical analysis, but either is useful as a control for detecting samples not worth chemical analysis. K. R. C.

3489. **Determination of uranium in flotation concentrates and in leach liquors by X-ray fluorescence.** G. L. Smithson, R. C. Eager and A. B. VanCleave (Dept. of Chem., Univ. of Saskatchewan, Saskatoon, Canada). *Canad. J. Chem.*, 1959, **37** (1), 20–28.—Approximate results for U are obtained by direct measurement on flotation concentrates, but more accurate results are obtained by the use of an internal standard, *e.g.*, Sr or Y. This method is

shorter than the conventional chemical or fluorimetric ones. Uranium in the organic phases obtained in liquid - liquid extraction studies can be determined. An aq. soln. of the internal standard is added to the sample, dispersion is facilitated by the addition of abs. ethanol, the sample is dried and ground for 30 min. and the significant part of the X-ray spectrum is recorded or determined by setting the spectrogoniometer at 2θ angles and counting for 100 sec. The background count at the position of the peak is interpolated from the background count on either side of the peak. Uranium in organic solvents is determined by the use of Br, added as bromobenzene, as the internal standard. The lower limit of determination of U_3O_8 is $\simeq 0{\cdot}02\%$ in solids and 0·1 mg per ml in soln. Iron in flotation concentrates and leach liquors can be similarly determined. S.C.I. ABSTR.

3490. **Determination of UO_3 and U_3O_8 in brown oxide.** L. G. Stonhill (Metall. Lab., Eldorado Mining and Refining Ltd., Ottawa, Canada). *Canad. J. Chem.*, 1958, **36** (11), 1487–1492.—"Brown oxide", produced by the incomplete reduction of UO_3 with H, is a mixture of UO_3, U_3O_8 and UO_2. Its content of UO_3 can be obtained by the extraction (for $\simeq 15$ min.) of 325-mesh material with hot 5% ammonium citrate soln. and determination of the loss in weight of the sample. The UO_3 and U_3O_8 in a fresh sample can be dissolved in 50% (v/v) H_3PO_4 at 100° in an atmosphere of CO_2, and the total U^{VI} can be titrated potentiometrically (in the same flask) with dil. $Ti_2(SO_4)_3$ in H_2SO_4 at 80° to 85° in the presence of $FeSO_4.(NH_4)_2SO_4$ ($\simeq 0{\cdot}25$ g). The UO_3 equiv. to the U_3O_8 can then be calculated, and hence the content of U_3O_8 and, by difference, of UO_2. The value for total U, calculated from the three results, is in good agreement with that given by the gravimetric and colorimetric methods, respectively. W. J. BAKER

3491. **Polarographic estimation of soluble silica in uranyl nitrate.** A. K. Sundaram and M. Sundaresan (Anal. Div., Atomic Energy Estab., Trombay, Bombay, India). *Anal. Chim. Acta*, 1958, **19** (6), 601–603.—Soluble silica is determined by the addition of ammonium molybdate to an acid soln. and polarographic determination of the molybdosilicate. *Procedure*—To 2·5 ml of NH_4NO_3 soln. (4 *N*), 0·5 ml of ammonium molybdate soln. (5%), 0·2 ml of HNO_3 (9·2 *N*) and 0·2 ml of gelatin soln. (0·05%) in a 10-ml flask add 1 g of sample dissolved in 2 ml of H_2O and dilute to 10 ml. Record the polarogram from 0 to $-0{\cdot}15$ V *vs.* the mercury pool. A blank is carried out in the basal soln. free from uranyl nitrate. Results are within $\pm 10\%$ for 10 to 100 p.p.m. of SiO_2; Cu, Fe (>1 p.p.m.) and V (>5 p.p.m.) interfere, but interference due to Cu can be eliminated by adding 2 ml of satd. salicylic acid soln., which also minimises interference from Fe. T. R. ANDREW

3492. **Colorimetric determination of fluorine.** A. A. Guntz and M. Arène (Lab. de Chim. Appl., Fac. des Sciences, Algiers). *Chim. Anal.*, 1958, **40** (12), 453–457.—The empirical thorium alizarinsulphonate method previously described (*cf. Anal. Abstr.*, 1958, **5**, 3729) has been studied with respect to the effect of pH, of the concn. of reagents and of the influence of Cl^- and SO_4^{2-}, results being presented as graphs. Working at pH 2·9 (0·02 *M* chloroacetic acid, semi-neutralised) and a constant concn. of Na alizarinsulphonate (51·3 mg per litre), the Th - F ratio is <1 for low extinctions and >1 for high ones, and a nomogram is given for the calculation of F, related to Th and extinction. Sulphate interferes by competing with F for the Th in the lake, but the total decrease in extinction is smaller than the sum of those due to the two ions separately. A nomogram is given from which, given the SO_4^{2-} (determined turbidimetrically) and the extinction, the F can be obtained. Under the given conditions, Cl^- do not interefere if the concn. is <10 g per litre. Fluorine in six Algerian waters ranges from 0·08 to 1·10 mg per litre. R. E. ESSERY

3493. **Rapid complexometric titration of fluoride ion.** S. Wilska (Dept. of Chem., Inst. of Technol., Helsinki, Finland). *Suomen Kem., B*, 1958, **31** (12), 400–401.—The usual complexometric method, which is based on pptn. of CaF_2 and back-titration of the excess of Ca^{2+} with EDTA, is modified so that the determination can be performed in 5 min. E. SJÖSTRÖM

3494. **Determination of fluoride by conductimetric titration.** H. Kubota and J. G. Surak (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 283–286.—The reaction between fluoride and lanthanum ions is used in this semi-micro determination in which the end-point is located by changes in the conductivity of the reaction medium. Milligram quantities of fluoride in solution can be determined with good accuracy and precision, if the total amount of extraneous ions is small. A modified semi-micro distillation apparatus is employed to carry out a distillation at constant temp. and vol., and this distillation minimises the amount of extraneous ions present in the titration medium. K. A. PROCTOR

3495. **Chlorine in distilled water as a source of laboratory error.** W. T. Caraway (McLaren Gen. Hosp., Flint, Mich., U.S.A.). *Clin. Chem.*, 1958, **4** (6), 513–518.—Distillation of chlorinated tap water may result in significant contamination of the distillate with free chlorine. The detection of free Cl and its effect on a number of the usual clinical laboratory determinations are discussed. H. F. W. KIRKPATRICK

3496. **Use of methyl chloride for the mass-spectrometric analysis of chlorine isotopes.** W. Herzog and E. Dörnenburg (Max Planck Inst. Chem., Mainz, Germany). *Z. Naturf.*, 1958, **13a**, 51–52.—Methyl chloride is especially suited for the analysis of chlorine isotopes with the mass spectrometer because this compound does not show any memory effects. After conversion of the Cl to be analysed into AgCl, the AgCl was reduced at 600° in a stream of hydrogen and the HCl formed was absorbed in aq. NH_3. By evaporation of the soln., the NH_4Cl used as starting material for an analysis was obtained. By treating 50 mg of NH_4Cl with 5 ml of a mixture of H_2SO_4 (240 ml), H_2O (40 ml) and methanol (350 ml) a small amount of methyl chloride is formed, which is transferred to the mass spectrometer. The amount of gas formed from 10 mg of NH_4Cl during 10 min. at 80° is sufficient to determine the isotope distribution in chlorine to within 0·5%. CHEM. ABSTR.

3497. **A spot test for chloride.** E. Phillips (Douglas Aircraft Co. Inc., El Segundo, Calif., U.S.A.). *Chemist Analyst*, 1958, **47** (4), 102.—For the detection of Cl^- or Br^- on corroded metal surfaces, immerse filter-paper in 0·25 *M* $AgNO_3$ in 0·1 *M* HNO_3. Apply the wet paper to the sample

surface, cover with a polyethylene film, and press on the surface for 5 min. Remove the paper and expose it to ultra-violet radiation or strong sunlight. A red, purple or grey discoloration on the paper indicates Cl^- or Br^-; I^- and F^- do not respond to the test. Interfering anions are those that give dark or highly coloured compounds with Ag (*e.g.*, sulphide, chromate). R. E. ESSERY

3498. **Micro-determination of chloride by non-aqueous potentiometric titration.** D. T. Lefferts (Colgate-Palmolive Co., Jersey City, N.J., U.S.A.). *Microchem. J.*, 1958, **2** (2), 257–261.—The anhydrous character of glacial acetic acid together with its ability to sharpen the end-point of the potentiometric curve make it a suitable medium for the direct argentimetric titration of Cl^- with a silver - glass electrode system and a pH meter. The method described permits the titration with 0·003 *N* $AgNO_3$ of 0·4 to 5·0 mg of Cl^- in 25 to 150 ml of glacial acetic acid. D. F. PHILLIPS

3499. **Rapid constant-current potentiometric titration of chloride ion. Use of polarisable platinum electrodes.** R. W. Freedman (Consolidation Coal Co., Res. and Devel. Div., Library, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 214.—The method described has been developed for determining Cl^- in water-soluble and oil-soluble organic materials. It can be used to determine any ion that yields silver salts of low solubility under standard conditions. K. A. PROCTOR

3500. **Spectrophotometric determination of microgram quantities of chloride and fluoride in metal oxides, salts and solutions.** B. D. La Mont and B. W. Conroy (Westinghouse Electric Corp., Atomic Power Dept., Pittsburgh). *U.S. Atomic Energy Comm.*, Rep. WCAP-918, 1958, 19 pp.—Nuclear power reactors and high-pressure boilers constructed of stainless steel are subject to stress corrosion in the presence of F^- and Cl^- in oxygenated systems. Consequently, determinations are made for Cl^- (0·5 to 15 μg) and F^- (0·5 to 50 μg). A procedure involving bleaching of the mercury - diphenylcarbazone complex is used to determine the Cl^-. Fluoride is measured by the bleaching of the thorium - thoron complex. These procedures were successfully applied to samples of metal oxides, salts and solutions. NUCL. SCI. ABSTR.

3501. **Quantitative determination of perchlorate ion in solution.** G. M. Nabar and C. R. Ramachandran (Dept. of Chem. Technol., Univ. of Bombay, India). *Anal. Chem.*, 1959, **31** (2), 263–265.—The method is based on the reaction between a known excess of methylene blue (**I**) and a soluble perchlorate. Sparingly soluble methylene blue perchlorate (**II**) is formed and is removed by filtration. The excess of **I** is determined colorimetrically in the filtrate. The small amount of **II** which is dissolved introduces a constant error, for which a correction is applied. Interference is caused by the presence of $Cr_2O_7^{2-}$, SO_4^{2-}, MnO_4^-, MoO_4^{2-} and IO_4^-, since these anions form ppt. with **I**. F. L. SELFE

3502. **Determination of bromate and periodate in the presence of each other.** L. Szekeres (Chem. Inst., Agric. Univ., Budapest, Hungary). *Z. anal. Chem.*, 1959, **165** (1), 32–36.—Two methods of determining BrO_3^- and IO_4^- in mixtures are developed. First, the sum of the two anions is determined iodimetrically in an aliquot. In one method (*a*), the anions are then reduced with HBr, BrO_3^- giving elementary Br, and IO_4^- giving IO_3^-. The Br is converted into Br^- (alkaline urea or H_2O_2) and the remaining IO_3^- are determined with $Na_2S_2O_3$. This method is preferred for low concn. of BrO_3^-. In the other method (*b*), IO_4^- are reduced with aq. H_2O_2 - $NaHCO_3$ to IO_3^-, the excess of H_2O_2 is destroyed, and BrO_3^- plus IO_3^- are determined with $Na_2S_2O_3$. This method is preferred for low concn. of IO_4^-. Results accurate to within ±1% are obtained for mixtures containing 5 to 30 ml of 0·1 *N* KIO_4 and 5 to 30 ml of 0·1 *N* $KBrO_3$. J. P. STERN

3503. **Inhibition of the catalytic effect of iodine on the system ceric sulphate - arsenous acid.** R. J. Magee and H. Spitzy (Paracelsus Inst., Bad Hall, Austria). *Mikrochim. Acta*, 1959, (1), 101–106.—Quadrivalent Ce gives a stable colour with brucine acetate in H_2SO_4 soln. only after development for 10 to 12 min. at 105°. The application of this reaction to the micro-determination of iodine in blood serum by means of its inhibitory effect on the $Ce(SO_4)_2$ - As_2O_3 reaction (*cf.* Spitzy *et al.*, *Anal. Abstr.*, 1959, **6**, 658) introduces undesirable complications. T. R. ANDREW

3504. **Chelometric analysis of manganese - magnesium and manganese - magnesium - zinc mixtures. Fluoride ion as a demasking agent.** W. G. Scribner (Res. and Engng Div., Monsanto Chemical Co., Dayton, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 273–275.—The fluoride ion demasks Mg selectively from a mixture of the chelates of Mn, Mg and Zn with EDTA. This makes possible a rapid analysis of Mn - Mg and of Mn - Mg - Zn mixtures, as required in the analysis of ferrites. *Procedure*—Dissolve the ferrite sample in HCl. Remove Fe by extraction of Fe cupferrate into benzene - *iso*amyl alcohol (1:1). Separate the aq. phase, add hydroxyammonium chloride (0·2 g) and adjust the pH to 10 with aq. NH_3 soln. (1:1). Add Eriochrome black T - NaCl (1:200), warm to 40° and titrate with standard EDTA soln. (disodium salt). The titration gives total bivalent metal ions. After the end-point, add 2 to 3 g of solid NaF and stir for 1 min. From a burette, add standard Mn soln., 1 ml at a time, until a permanent red colour is obtained. Stir for 1 min. and titrate the excess of Mn with standard EDTA soln. The amount of standard Mn soln. equivalent to the Mg present is thus obtained. After the second end-point, if Zn is present, add KCN (2 ml of a 10% soln. for every millimole of Zn) to displace Zn from its chelate. From a burette add an excess of standard Mn soln., then titrate the excess of Mn with standard EDTA soln. Calculate the Zn content of the mixture. The Mn content of the original sample is obtained by difference. The analysis of a ternary mixture can be completed in <40 min., including calculations. The error is generally <0·1 mg of each metal. Extensions of the method to other metal combinations are suggested. F. L. SELFE

3505. **Co-precipitation and ion-exchange adsorption of technetium.** Niro Matsuura, Masuo Kojima and Akira Iguchi (Fac. of Gen. Educ., Tokyo Univ., Komaba, Meguro-ku). *Japan Analyst*, 1958, **7** (12), 792–794.—Co-pptn. of Tc in the form of $KTcO_4$ was examined with CuS, CdS, FeS and As_2S_3. Co-pptn. with CuS from 0·3 *N* HCl appears to be the best method for the collection of Tc. In HNO_3 or $HClO_4$ soln., a mono - monovalent adsorption is observed with Dowex 1X-8 (Cl)

(50 mesh). Technetium seems to be adsorbed as $HTcO_4$, most of which is readily eluted with 0·5 *M* $HClO_4$, a small residual amount of Tc being only very slowly eluted. K. Saito

3506. **Spectrophotometric determination of perrhenate.** J. B. Headridge (Chem. Dept., Univ., Sheffield, England). *Analyst*, 1958, **83**, 690–691.—In a proposed method for the determination of rhenium in organic rhenium complexes containing N, the samples are oxidised by fusion with Na_2O_2 in a micro Parr bomb and the final acidified soln. contains Na, H, Cl^-, NO_3^- and perrhenate ions. For determination of perrhenate, the u.v. spectrum of potassium perrhenate in the presence of other ions was investigated. The molar extinction coeff. is 3610 at 228 mμ and 6060 at 206 mμ. Appreciable absorption by Cl^- starts only below 210 mμ; NO_3^- has an absorption peak at 303 mμ and a minimum at 264 mμ. The absorption peak at 228 mμ can be used for the determination of perrhenate in soln. containing no other ions that absorb appreciably at this wavelength, and the plot of linear extinction *vs.* concn. over the range 0 to 50 p.p.m. of Re passes through the origin. The optimum wavelength for the determination in the presence of both Cl^- and NO_3^- is 258 mμ over the range 0 to 250 p.p.m. of Re in a 0·65 *M* soln. of NaCl. The intercept of this graph on the extinction axis represents the slight absorption of the NaCl. With application of the appropriate corrections for Cl^- and NO_3^-, this method provides a rapid means of determining perrhenate in simple soln.

A. O. Jones

3507. **Volumetric determination of iron(III) with hydroxylamine as reducing agent.** G. Gopala Rao and G. Somidevamma (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1959, **165** (6), 432–436 (in English).—Ferric iron is reduced to Fe^{2+} with excess of hydroxylamine at an acidity of 0·2 to 0·5 *N* with respect to H_2SO_4 and at a temp. of 100°. The soln. is cooled, the acidity is made 6 *N*, and the Fe^{2+} are titrated with sodium vanadate soln., with N-phenylanthranilic acid as internal indicator. The precision is within ±0·2%. G. P. Cook

3508. **Photometric determination of iron(III) employing 1:2-diaminocyclohexanetetra-acetic acid.** F. Bermejo Martinez and R. Rey Mendoza (Univ. of Santiago de Compostela, Spain). *Chemist Analyst*, 1958, **47** (4), 94–95.—Prepare a 5% aq. soln. of 1:2-diamino*cyclo*hexanetetra-acetic acid by dissolving the acid in the required amount of NaOH soln. and neutralising with HCl, or by using the disodium salt. Into a 25-ml flask place an aliquot of the sample soln. such that the final concentration of Fe will be in the range 30 to 250 μg per ml, and add 3 ml of reagent soln., followed by 2 *M* NaOH drop by drop till pH 4 is reached (pH meter or indicator paper). Dilute to 25 ml, mix, and measure the absorption in a photo-electric colorimeter against a water blank, using an indigo filter. Refer results to a standard curve. Cations that form coloured complexes with the reagent (Cu^{II}, Ni^{II}, Mn^{II} and Co^{II}) interfere. At pH 4, the colour is stable to light for at least 10 days. A small excess of reagent does not interfere, but a large excess should be avoided, owing to the limited solubility of the free acid at pH 4.

R. E. Essery

3509. **Spectrophotometric study of the cyanomalonate ion. Application to the spectrophotometric determination of the ferric ion.** G. Mignonac, R. Miquel and C. Bonnemaison (Lab. de Chim. Gén., Fac. des Sci., Toulouse, France). *Bull. Soc. Chim. France*, 1958, (11–12), 1323–1330.—Diethyl cyanomalonate (**I**) is prepared by the action of ClCN on diethyl sodiomalonate. Its absorption spectrum in the u.v. (max. at 214 and 247 mμ) at various pH values is measured and the p*K* shown to be 1·3. When **I** is caused to react with Fe^{3+} at pH 2·8 to 3·8 and extracted with $CHCl_3$, a complex with max. at 504 mμ and absorption coeff. of 3600 is obtained. The nature of the complexes with Fe^{3+} is investigated and by pptn. in aq. soln. a complex approximating to X_2FeOH (X = **I**) is obtained. By extraction in $CHCl_3$, complexes with compositions FeX_3 and FeX_4H are obtained. *Procedure for determination of Fe^{2+} and Fe^{3+} simultaneously*—An acid soln. of the two ions is adjusted to pH 3 to 4 with Na acetate and then a slight excess of a reagent, consisting of 1:10-phenanthroline (0·2 g), 0·1 *M* diethyl ammoniocyanomalonate (**II**) (5 ml), glacial acetic acid (5 ml) and water to 25 ml, is added. The Fe^{3+} complex is extracted with $CHCl_3$ and measured spectrophotometrically, and the Fe^{2+} complex with 1:10-phenanthroline is measured similarly in the aq. layer. This gives low results for Fe^{3+} with a relative error of $< 5\%$. *For determination of Fe^{2+}*—To a sample of Fe^{2+} (0·7 to 11 μg) at pH 2·8 to 4 is added a slight excess of 0·1 *M* **II** (at least 4 molar proportions), and after a few minutes the complex is extracted into $CHCl_3$ and the absorption measured (with a filter, between 460 and 520 mμ). A similar semi-micro method is described. E. J. H. Birch

3510. **Polarographic determination of iron and manganese in ores and metallurgical products.** I. M. Issa, R. M. Issa and I. F. Hewaidy (Dept. of Chem., Univ. of Egypt, Giza). *Chemist Analyst*, 1958, **47** (4), 88–90.—In the polarographic determination of Mn in triethanolamine, the use of Na_2SO_3 to remove dissolved O and excess of H_2O_2 (used as an oxidant) permits Fe and Mn to be determined in the same soln. Transfer the soln. containing Fe and Mn to a 25-ml flask containing 8 ml of 50% triethanolamine. Add sufficient 5 *M* NaOH to make the soln. 0·5 *M* when diluted to the mark. Add a little water and bubble air for 5 to 10 min., or add a few drops of H_2O_2 and mix. Dilute to 25 ml, transfer 10 ml to the polarograph cell, and bubble N for 15 min. If H_2O_2 has been used, set aside for 30 min., or add 0·2 g of Na_2SO_3. Record the polarogram, read the diffusion currents for the first and second waves, and refer results to standard curves for Fe and Mn, respectively. For the determination of Mn in steel or cast iron, 1 g of sample is dissolved in 10 ml of 50% HNO_3, the soln. is filtered, filtrate and washings are made up to 100 ml and 10 ml is treated as described above, only the Mn wave being recorded. For Fe and Mn in ores, 1 g is dissolved in 50% HNO_3 with a little H_2O_2, the soln. is fumed with H_2SO_4, diluted with water, filtered, and made up to 250 ml, 10 ml being treated as described above. Results agree well with those by classical methods. R. E. Essery

3511. **Determination of metallic iron, iron oxides, iron carbide and free carbon in iron catalyst treated with carbon monoxide.** Yoshio Murata and Shigeaki Kasaoka (Fac. of Educ., Univ. of Osaka Prefecture, Sakai). *Japan Analyst*, 1958, **7** (11),

721–724.—Total carbon is determined by the combustion method (*cf.* Touhey and Redmond, *Anal. Chem.*, 1948, **20**, 202). The sample (300 mg) is boiled with H_2SO_4 (1:10, 100 ml) for 30 min., then filtered, and the residue is dried and used for the determination of free carbon by the combustion method. Total iron and ferrous iron are determined by the mercuric chloride - iodine method (*cf. Anal. Abstr.*, 1956, **3**, 3049; 1958, **5**, 3743). K. SAITO

3512. **Combustion method for determination of sulphur in ferrous alloys. Modifications for minimising errors.** J. W. Fulton and R. E. Fryxell (Transformer Div., General Electric Co., Pittsfield, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (3), 401–405.—Losses in the combustion method for determining S in metals have been studied by the use of ^{35}S. Above 1550°, only 1 to 2% of the total S remains in the slag; most of the loss occurs by adsorption on the glassware of the delivery system. A further loss is due to formation of SO_3, which is not titrated by KIO_3. By using a temp. of 1550°, a shortened delivery system, and an O flow of 5 litres per min., results of 92% of the theoretical are obtained when the gases are absorbed in H_2O_2, rinsings from the delivery system added, and the whole titrated with NaOH soln. to a bromocresol purple end-point. The value as titrated times a loss factor of 1·09 gives good precision and accuracy over the range 0·01 to 0·272%. For S contents > 0·01%, rinsings and blank may be ignored.

P. D. PARR-RICHARD

3513. **4:4′-Substituted 2:2′-dipyridyls in chelation reactions with ferrous iron.** G. F. Smith and W. M. Banick, jun. (Noyes Chem. Lab., Univ. of Illinois, Urbana, U.S.A.). *Analyst*, 1958, **83**, 661–666.—The mol. extinction coeff. and wavelengths of max. absorption have been determined for the Fe^{2+} complexes of eleven 4:4′-derivatives of 2:2′-dipyridyl, *viz*, those with $-CH_3$ (**I**), $-C_2H_5$ (**II**), –Br (**III**), –Cl (**IV**), $-OCH_3$ (**V**), $-OC_2H_5$ (**VI**), $-OC_6H_5$ (**VII**), $-COOC_2H_5$ (**VIII**), $-CONH_2$ (**IX**), –COOH (**X**) and $-NO_2$ (**XI**) as substituents. Procedures for ascertaining the optimum pH for formation of the chelate complexes and their extraction are described. The spectrophotometric data assign the reagents to 3 groups, *viz*, unsubstituted 2:2′-dipyridyl and ligands **I**, **II**, **III** and **IV**; **V**, **VI** and **VII**; and **VIII**, **IX** and **X**. As with the Fe^{2+} complexes of the 1:10-phenanthrolines, attempts to use the u.v. absorption for determination of Fe failed owing to interference from the necessary excess of ligand present. In certain circumstances it might be possible to use ligands **II**, **VI**, **VII** and **VIII** (and 4:4′-diphenyl-2:2′-dipyridyl), which absorb negligibly at 340, 330, 340 and 350 (and 356 mμ), respectively, whereas their respective Fe complexes absorb at 355, 359, 363 and 384 (and 386 mμ). All the Fe^{2+} complexes as well as the excess of ligand are extractable. This restricts their use in analysis except in special circumstances.

A. O. JONES

3514. **Direct titration of ferricyanide in the presence of zinc sulphate. Determination of nitrite.** B. R. Sant (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (6), 523–524.—Potassium ferricyanide soln. (*M*) heated to boiling in the presence of Zn^{2+} may be quant. titrated with NO_2^-, at a pH of 6 to 7, or in soln. of higher alkalinity up to about 0·3 *N* NaOH. The end-point is shown by complete decolorisation of the soln. The method may be used for the determination of NO_2^-.

T. R. ANDREW

3515. **Proximate method of spectral analysis of austenitic steel.** A. G. Komarovskiĭ. *Tsent. Nauch.-Issled. Inst. Tekhnol. i Mashin.*, 1957, **84**, 199–225.—The effect of a third metal on the spectroscopic analysis was studied in spark, arc and a.c. arc discharges of binary alloys of Fe with Si, Mn, Cr, Ni, Mo, W, Ti, V, Co, Al, B and Nb and of complex high-alloyed steels. The results were plotted on log (I_p/I_1) and log *C* co-ordinates, where I_p and I_1 are the line intensities of the element sought and the comparison element (Fe) and *C* is the concn. (wt. %) of the element sought. The regularity of the principle of the parallel shift of the calibration lines caused by the presence of the third element was established for different types of steel. The coeff. of parallel shift classified the metals into a few groups, reducing the number of standards needed. The accuracy of determination of an element was within 2·5 to 5·1% and the analysis was completed within 10 min. Working curves of all elements and tables of line-pairs of spectral lines are given. The processes within the clouds of the spark affected by the duration ("effect of firing") were investigated. Only the determination of Mn, Cr, Al and Nb was affected by the "effect of firing." Analyses in atmospheres of air, N and O showed that this effect was due to oxidation. CHEM. ABSTR.

3516. **Rapid determination of various non-metallic inclusions in steel.** Takuho Ikegami and Ohiko Kammori (Tech. Res. Inst., Yawata Iron and Steel Works, Fukuoka-ken). *Japan Analyst*, 1958, **7** (10), 636–640.—In order to minimise the time taken for electrolysis, the amount of the sample is reduced to 10 g and the non-metallic inclusions are fused with Na_2CO_3 (3 g); the melt is dissolved in water (50 ml), and made acid with H_2SO_4 (1:5, 15 ml) and a few drops of 10% hydroxyammonium sulphate soln. The insol. residue is fused with $K_2S_2O_7$ and then dissolved in dil. H_2SO_4. The combined soln. are made up to 250 ml and the following components are determined colorimetrically with the following reagents—Si with $(NH_4)_2MoO_4$; Al with aluminon (Cr and Fe being removed by mercury cathode electrolysis); Fe with nitroso-R salt; Mn with $(NH_4)_2S_2O_8$; Ti with H_2O_2; Cr with diphenylcarbazide.

K. SAITO

3517. **Hydrogen in steel.** B. A. Shmelev. *Tsent. Nauch.-Issled. Inst. Tekhnol. i Mashin.*, 1957, **84**, 12–40.—Methods of determining H in steel are discussed and a method of sampling and storing specimens is outlined. The molten metal is drawn into quartz tubes (8 to 9 mm inside diam.), constricted every 20 to 25 mm. After quenching in water the tube is broken at the constrictions and the specimens are stored under glycerol. Hydrogen is determined by electrolytic saturation in two cells in series, with the specimen as a cathode in one and a platinum wire in the other. The H absorbed is measured by the difference in vol. of displaced electrolyte in both cells. After saturation, the specimen is stored in glycerol and the H evolved in ageing is determined by the vol. of glycerol displaced. The specimen is then analysed for H *in vacuo*. CHEM. ABSTR.

3518. **Hydrogen in ferrosilicon. Analytical methods and average hydrogen contents of some commercial grades.** N. Christensen and K. Gjermundsen. *J. Iron St. Inst.*, 1958, **190** (3), 248–254.—The presence of hydrated lime and alumina was found to give severe segregation of H, and the H content increased with decreasing particle size of the sample, increasing exposure to air and rapidity of analysis after manufacture. The limitations of the vacuum-fusion procedure are discussed. J. W. O. PYEMONT

3519. **Spectrophotometric determination of magnesium in cast iron with xylidyl blue.** Takuho Ikegami, Ohiko Kammori and Takayuki Jitsumatsu (Tech. Res. Inst., Yawata Iron and Steel Works, Fukuoka-ken). *Japan Analyst*, 1958, **7** (10), 641–644.—Mann and Yoe's colorimetric determination of Mg with xylidyl blue (**I**) (*cf. Anal. Abstr.*, 1956, **3**, 2009) was applied to the rapid (90 min.) analysis of cast iron. There is no interference from $< 80 \mu g$ of Al, Ti, As, Mn and Ca, which remain in soln. after the electrolytic separation of Fe with a mercury cathode. The excess of H_2SO_4 is removed by heating; $HClO_4$ can be used in its place. *Procedure*—Dissolve the sample (0·1 g) in H_2SO_4 (1:9, 5 ml) and H_2O_2 (15%, 10 ml), boil, filter off and wash the ppt. with H_2SO_4 (1:100) and remove Fe from the filtrate by electrolysis with a mercury cathode. Evaporate the soln. until white fumes cease to appear. Dissolve the residue in 100 ml of water and to a 5-ml aliquot add **I** (0·015% in ethanol, 5 ml) and $Na_2B_4O_7$ soln. (0·08 *M*, 0·5 ml) and dilute to 25 ml with water. Measure the extinction at 470 mμ, with a reference soln. containing the same amounts of **I** and $Na_2B_4O_7$. K. SAITO

3520. **Quick method for the determination of lead in steel.** S. Meyer and O. G. Othmar (Neunkircher Eisenwerk A.-G., Neunkirchen, Saar). *Arch. Eisenhüttenw.*, 1958, **29** (11), 677–681.—Three rapid methods are developed in which Pb is separated as $PbSO_4$, or gravimetrically determined as $PbMoO_4$ or $PbCrO_4$. With the first method results are obtained within 2 to 2·5 hr., the mean error being $\simeq 0{\cdot}001\%$ for 0·2% of Pb. Photometric determinations were also found to be suitable. The Pb is directly determined in the test soln. as PbI_2. Single determinations can be made in 45 min., with a standard deviation of $\pm 0{\cdot}003$ for contents of Pb of $\simeq 0{\cdot}2\%$. L. M. RIEGELHAUPT

3521. **Effect of temperature on the spectrophotometric determination of phosphorus in iron and steel by the molybdovanadophosphate method.** Hiroshi Kitagawa and Norio Shibata (Hitachi Cent. Res. Lab., Kokubunji, Tokyo). *Japan Analyst*, 1958, **7** (12), 788–789.—The temperature coeff. of the extinction of molybdovanadophosphate in $HClO_4$ soln. (*cf.* Baghurst and Norman, *Anal. Abstr.*, 1956, **3**, 82) is markedly decreased by the addition of ethanol (15 ml per 100 ml of the final soln.) or Na_2SO_4 (2 g). K. SAITO

3522. **Methods for the analysis of steel. Part 9. Phosphorus in high chromium - nickel steels.** British Standards Institution (2 Park Street, London). B.S. 1121: Part 9: 1948, incorporating amendment November, 1957, 9 pp.—The original method was developed for use on high Cr - Ni steels and other highly alloyed steels and depended on the oxidation of the Cr in soln. by fuming with $HClO_4$ for 10 min., followed by reduction with HBr. Phosphorus is pptd. from cold soln. with nitromolybdate and the ppt. is converted into $PbMoO_4$, which is weighed. The amendment provides for the determination of P in all steels by raising the fuming temperature until $HClO_4$ refluxes on the walls of the beaker for 10 to 15 min. The subsequent procedure is unaltered. J. O. LAY

3523. **Removal of sulphuric acid from phosphoric acid used for the determination of sulphur in high-chromium steel.** Hiroshi Kitagawa and Norio Shibata (Hitachi Central Res. Lab., Kokubunji, Tokyo). *Japan Analyst*, 1958, **7** (9), 587–588.—Sulphuric acid in commercial H_3PO_4 (sp. gr. 1·7) is readily removed by heating with metallic chromium (0·2 g for 10 ml of H_3PO_4) at $>250°$ for 30 min. and does not then increase the blank value for the determination of S by the H_2S method. Sulphuric acid is also satisfactorily removed by the tin - phosphoric acid method (*cf.* Kiba *et al.*, *Anal. Abstr.*, 1956, **3**, 2708; Kiba and Kishi, *Ibid.*, 1957, **4**, 3305). K. SAITO

3524. **The oxidation of chromium [in steel] with perchloric - phosphoric acid. A study by the Box - Wilson method.** Hiroshi Kitagawa and Norio Shibata (Hitachi Central Res. Lab., Kokubunji, Tokyo). *Japan Analyst*, 1958, **7** (10), 619–623.—Optimum conditions for the oxidation of Cr in low-alloy steel with $HClO_4$ and H_3PO_4 were studied by the Box - Wilson statistical method (*J. R. Statist. Soc., B*, 1951, **13**, 1), and were found to be—ratio of H_3PO_4 to $HClO_4$, $0{\cdot}4 \pm 0{\cdot}05\%$ (v/v); temp., 203° ± 1°; time of oxidation, $3{\cdot}5 \pm 0{\cdot}5$ min. For the reduction of simultaneously oxidised Mn, NaN_3 (Willard and Young, *J. Amer. Chem. Soc.*, 1929, **51**, 139) is the best reductant. *Procedure for low-alloy steel*—Dissolve the sample (0·2 to 1 g) in mixed acid ($HClO_4$, 500 ml; H_3PO_4, 200 ml; HNO_3, 100 ml; and water, 200 ml) (20 to 40 ml), heat at 202° to 204° for 3 to 4 min., dilute fourfold, boil with NaN_3 soln. (2%, 0·1 to 0·5 ml) and titrate with 0·033 *N* $FeSO_4$ and $KMnO_4$ by the usual method. K. SAITO

3525. **Photometric determination of manganese in steel and cast iron.** J. E. Bolzan (Lab. Quim.-Metalurg., Ferrocarril General Roca, Remedios de Escalada, Argentina). *Chemist Analyst*, 1958, **47** (4), 95–96.—The modified persulphate - silver method eliminates the error due to foreign ions by using a bleached blank. Dissolve the sample (50 mg) in 5 ml of acid mixture (150 ml of conc. H_2SO_4, 150 ml of conc. H_3PO_4, 700 ml of water) by heating in a glycerol bath. When dissolution is complete, oxidise with a few drops of conc. HNO_3 and heat to expel nitrous fumes. With cast iron, dilute to reduce the acidity and filter off the graphite. Then add 2 ml of 1% $AgNO_3$ soln. and 2 ml of satd. $(NH_4)_2S_2O_8$ soln., boil for 2 to 3 min. in a glycerol bath to expel oxygen, then cool rapidly in tap water and make up to 25 ml. Read the absorption in a test-tube cell against water, in a colorimeter with a logarithmic scale, and with a green filter. Add to the cell 1 to 2 drops of 0·3% H_2O_2 to bleach the permanganate, and read the absorption due to other ions. All cells should be matched to a position of min. absorption with water, and the sample should be analysed concurrently with a similar material of known Mn content. The total permanganate reading, corrected for the bleached blank, is proportional to the Mn content. Recoveries from a standard cast iron and 4 standard steels were satisfactory. R. E. ESSERY

3526. **Determination of low cobalt contents in ores, pig iron and steel.** G. Graue, S. Eckhard and W. Gradtke (Phoenix-Rheinrohr A.-G., Duisburg-Ruhrort, Germany). *Angew. Chem.*, 1959, **71** (1), 28–30.—The high neutron-capture cross-area of Co necessitates the accurate determination of small quantities of Co in materials to be subjected to irradiation. This is best done photometrically with nitroso-R salt. Iron interferes and is removed by extraction into di*iso*propyl ether as $FeCl_3$ or preferably by pptn. as basic oxide with ZnO (which also removes Cr, W, Mo, Ta, Ti, Nb, Zr, V and Cu). High accuracy is attained with Co contents of the order of 0·001 to 0·1%. Manganese causes low, and Cu high, results, and Cr interferes. Two methods are described. (*i*) Dissolve the sample (1 g) in HCl (1:1) (20 ml), oxidise with $KClO_3$ (1 g), evaporate to dryness, and dissolve the residue in HCl (3:1) (20 ml). If >0·5% of Si is present, filter. Concentrate to 20 ml, and extract with di*iso*propyl ether (4 × 30 ml). Evaporate the Fe-free aq. phase to dryness, dissolve in HNO_3 (2 ml), evaporate just to dryness, dissolve in HNO_3 (1:1) (10 ml), and add Na citrate - NaOH buffer at pH 6 to 6·5. Dilute to 50 ml, filter, treat 25 ml of the filtrate with 0·5% nitroso-R salt soln. (5 ml) and after 10 min. add HNO_3 (1:2) (5 ml). Dilute to 50 ml, shake, and measure the colour photometrically against a blank. Read the Co content from a calibration curve. (*ii*) Dissolve the sample (1 g) in HNO_3 (1:1) (10 ml), boil off N oxides, add H_2O_2 (1:1) (3 ml), boil for 2 min., dilute to 30 ml with H_2O, and add a suspension of ZnO (5 g). Boil briefly, dilute to 100 ml, shake, and filter. Determine the Co content of 50 ml of filtrate as described above, with a mercury lamp and a filter (Hg 546). Nickel (>2%) interferes. J. P. STERN

3527. **Determination of cobalt with 2-nitroso-1-naphthol.** H. Schüller (Landwirtschaftl.-Chem. Bundesversuchsanst., Vienna). *Mikrochim. Acta*, 1959, (1), 107–121.—The 'cold' procedure of Claassen and Daamen (*cf. Anal. Abstr.*, 1955, **2**, 3366) is preferred to the 'hot' procedure of Baron (*cf. Anal. Abstr.*, 1954, **1**, 489) since the interference of Mn can be readily eliminated in the former procedure. In the examination of agricultural material, platinum from laboratory ware acts as a contaminant. Four procedures are described for overcoming interference due to Pt—(*i*) ion-exchange separation of Pt as chloroplatinate on Dowex 2-X8 anion-exchange resin in 6 *N* HCl; (*ii*) extraction of Pt^{2+} with diphenylthiocarbazone at pH 1 to 2; (*iii*) a combined extraction and ion-exchange procedure applicable in the presence of large amounts of phosphate and inorganic salts; (*iv*) a 'correction' procedure by which the Co content may be deduced from measurements of the extinctions at 365 and 420 mμ without prior separation of Pt.

T. R. ANDREW

3528. **Spectrophotometric determination of cobalt with 1-(2-pyridylazo)-2-naphthol.** G. Goldstein, D. L. Manning and O. Menis (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 192–195.—The Co^{2+} chelate with 1-(2-pyridylazo)-2-naphthol is readily extracted into $CHCl_3$, the extract showing absorption peaks at 590 and 640 mμ. Fewer interferences are encountered when the extinction is measured at 640 mμ. Beer's law is obeyed over a range of 0·1 to 2·4 μg of Co per ml, with a coefficient of variation ≃3%. Interfering ions are Cu^{2+} (when Cu:Co > 1:1), Ni^{2+} (Ni:Co > 10:1), and Fe^{3+}, Zn^{2+} and Cd^{2+} (milligram amounts). Lesser amounts of these ions are readily masked by citrate. A procedure is given for the determination of Co in concn. from 0·1 to 10 p.p.m. in impure thorium oxide, and it is suggested that the method may also be applied to the determination of Co in steel and other alloys. A strong base anion-exchange resin is used to concentrate the Co and to separate it from Th and from interfering ions. In this separation, Co is adsorbed from a soln. 10 *M* with respect to HCl and is eluted with 4 *M* HCl. F. L. SELFE

3529. **Co-precipitation of cobalt(II) with zinc sulphide.** Hiroshi Hamaguchi and Toshi Kawashima (Chem. Dept., Tokyo Univ. of Educ., Koishikawa). *Japan Analyst*, 1958, **7** (10), 627–630.—Co-precipitation of Co^{II} with ZnS (investigated with ^{60}Co as tracer) is largely affected by the rate of flow of H_2S. At pH 2·5 only 0·5% of Co (≃0·02 *M* soln.) is co-pptd. when the rate of flow is <10 ml per min., whilst ≃25% of Co is co-pptd. when the flow rate is 200 ml per min. The use of thioacetamide (*cf.* Swift and Butler, *Anal. Abstr.*, 1956, **3**, 2061) does not prevent the co-pptn. K. SAITO

3530. **Use of diphenylglyoxime in the photometric determination of nickel.** Z. Gregorowicz (Inst. f. Anorg. Chem. d. Schlesischen Tech. Hochsch., Gliwice, Poland). *Acta Chim. Acad. Sci. Hung.*, 1959, **18** (1–4), 79–84 (in German).—Diphenylglyoxime (**I**) is particularly useful for the determination of Ni in soln. containing ethanol, when dimethylglyoxime cannot be used. To the nickel soln. in a 50-ml flask are added 5 ml of poly(vinyl alcohol) soln. (0·5% aq.), 6 ml of **I** soln. (0·02% in ethanol), 8 ml of satd. aq. iodine soln. and a few drops of 2 *N* aq. NH_3 soln. After being shaken for 2 min., the soln. is made up to volume and the colour is measured, a Pulfrich photometer with Zeiss S filters and 5-cm cells being used. A suitable range of concn. is 0·01 to 0·10 mg of Ni^{2+} per 50 ml.

H. M.

3531. **Gasometric determination of metallic nickel in the presence of nickel(II) oxide.** E. Krejcar (Res. Inst. Fats and Oils, Prague). *Chem. Listy*, 1958, **52** (12), 2410–2411.—The vol. of H liberated by dissolving a mixture of metallic nickel and NiO in acid, which is equiv. to the amount of metallic Ni, can be measured in a special apparatus (illustrated); in the upper part the vol. of H is measured and the lower part serves for the reduction of NiO and for the dissolution of the reduced Ni.

J. ZÝKA

3532. **Analysis of nickel sulphamate plating solutions.** G. H. Bush and D. C. Higgs (Armament Res. and Devel. Estab., Fort Halstead, nr. Sevenoaks, Kent, England). *Trans. Inst. Met. Finish.*, 1958–59, **36** (2), 43–47.—Examination of the effects of process variables on the physical properties of deposits of Ni from nickel sulphamate baths is described. Synthetic soln. of known composition were used. Determination of N by the Kjeldahl method showed that no catalyst was necessary; NH_4^+ were determined by distillation of an aliquot of the bath made alkaline with NaOH. Direct titration with EDTA (disodium salt), with murexide as indicator, was used for determining Ni. Boric acid was determined by titration with NaOH soln., in the presence of mannitol, after separation from Ni by passage through a cation-exchange column.

Naphthalene-1:3:6-trisulphonic acid was determined by measurement of the extinction of a diluted soln. at 280 mμ. Chloride was determined by the Volhard method after removal of Ni by means of an ion-exchange column. The method of calculating the results is given and the results are tabulated.
C. H. COWPER-COLES

3533. **Reduction of nickel(IV) dimethylglyoximate.** A. Okáč and M. Šimek (Inst. Anal. Chem., Masaryk Univ., Brno, Czechoslovakia). *Chem. Listy*, 1958, **52** (12), 2285–2291.—The stability of red soln. of oxidised Ni dimethylglyoximate described previously (*Chem. Listy*, 1958, **52**, 1903) has been studied potentiometrically and photometrically, with the use of various agents for the oxidation of dimethylglyoxime [bromine, iodine, $K_3Fe(CN)_6$ and O, in alkaline and aq. NH_3 soln.] and for the reduction of the reaction product (titration with $SnCl_2$). The red complex $[NiD_3]^{3-}$ is reduced to the yellow soln. of the bivalent Ni complex $[NiD_2]^{4-}$; both complexes are stable only in strongly alkaline soln., the latter only in an inert atmosphere. When neutralising alkaline soln., the salt of dimethylglyoxime $Ni(DH)_2$ is formed. The oxidation of Ni dimethylglyoximate in alkaline soln. to the red form must be carried out in alkaline soln. containing an excess of dimethylglyoxime.
J. ZÝKA

3534. **Spectrophotometric determination of ruthenium.** R. P. Larsen and L. E. Ross (Chem. Engng Div., Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 176–178.—Ruthenium is determined as perruthenate. Ruthenium tetroxide is distilled from a 6 *N* H_2SO_4 soln., containing 40 to 300 μg of Ru, in the presence of sodium bismuthate (0·5 g) as oxidant. The distillate is collected in ice-cold *N* NaOH containing NaClO (1 ml of 5% soln.). Distillation is complete in <5 min. The receiver is then warmed to room temp. and the soln. diluted to a known vol. with *N* NaOH. The extinction of the soln. is measured at 385 mμ against a reagent blank. Calibration must be checked daily. If this is done, a precision, at the 95% confidence level, of ±1·5% with a max. deviation of 2·0% is shown by 12 replicate determinations. The procedure has been applied to the determination of up to 5% of Ru in uranium-ruthenium alloys.
F. L. SELFE

3535. **Use of oscillographic polarography in quantitative analysis. IX. Identification and determination of rhodium in the presence of platinum, palladium and gold.** P. Beran and J. Doležal (Inst. Anal. Chem., Charles' Univ., Prague). *Chem. Listy*, 1958, **52** (12), 2403–2404.—The sensitive oscillographic determination of Rh in platinum, palladium and gold is based on the catalytic effect of Rh^{3+} (*Chem. Listy*, 1957, **51**, 1289). The depolarisation of Rh^{3+} on the dropping mercury electrode in acid medium is characterised by a sharp peak in the $dE/dt = f(E)$ oscillographic curves. Concn. of 0·02% of Rh in platinum and 0·005% of Rh in palladium and gold can be detected. The height of the peak corresponds to the concn. of Rh in the range of 0·5 μg to 25 μg in 20 ml of the electrolyte and can be used for quant. purposes. A calibration curve or the method of standard additions can be used for the evaluation of the results. *Procedure*—To the soln. of the sample containing 0·006 to 0·12 mg of Rh add *N* HCl (2 ml) and 4 *N* NaCl (3 ml), polarograph, and measure the height of the peak. A ration of Rh to Pt or Pd of 1:2000 and Rh to Au of 1:3300 has been determined with an accuracy of $\simeq \pm 5\%$.
J. ZÝKA

3536. **Fire assay for platinum and palladium in ores and concentrates.** M. E. V. Plummer, C. L. Lewis and F. E. Beamish (Div. of Anal. Res., Univ. of Toronto, Canada). *Anal. Chem.*, 1959, **31** (2), 254–258.—A new method is proposed for the recovery, separation and determination of Pt and Pd. A fire-assay fusion of the sample with Na_2CO_3 in a carbon crucible at 1450° yields an Fe - Ni - Cu alloy button, which contains the Pt and Pd present in the original sample. A sulphide phase (matte) and a slag are also formed, the matte containing only minor amounts of Pt and Pd and the slag none. The button is dissolved in HCl, and Pt and Pd are isolated by means of a cation-exchange resin; Pt and Pd are then separated by paper chromatography and, after extraction from the chromatogram, determined spectrophotometrically. The results compare favourably with those obtained by the classical fire-assay procedure.
F. L. SELFE

3537. **New approach to the analysis of brass, cadmium and zinc plating solutions, using ethylenediaminetetra-acetic acid and Fast Sulphon black F.** K. E. Langford. *Electroplating*, 1958, **11** (12), 439–441.—A rapid, accurate volumetric method is described. An aliquot (2 ml) of the plating soln. is evaporated to dryness in a 500-ml flask with 5 ml of conc. HCl and 5 ml of H_2O_2 (20 vol.). While the residue is still hot, 50 ml of H_2O and 20 ml of conc. aq. NH_3 are added and the mixture is filtered to remove Fe. Standard copper soln. (8 g of $CuCl_2.6H_2O$ per litre) (2 ml) is added (except for brass soln.) and the soln. is diluted to 400 ml; 6 to 8 drops of 1% Fast Sulphon black F (C.I. Acid Black 32) indicator are added and the soln. is titrated with 0·2 *N* EDTA (disodium salt) to a dull green end-point.
C. H. COWPER-COLES

3538. **Quantitative X-ray determination of anatase and rutile in mixtures.** J. Wańková (Res. Inst. Inorg. Chem., Ústí nad Labem). *Chem. Průmysl*, 1958, **8** (11), 577–580.—A selective method for the determination of the content of anatase and rutile in titanium white has been developed.
J. ZÝKA

3539. **Methods of testing refractory materials. Additional methods.** British Standards Institution (2 Park Street, London). Addendum No. 2 (1959) to B.S. 1902:1952. 8 pp.—Additional methods are specified for the determination of silica, size of refractory bricks and shapes, bulk density and warpage (convexity and concavity).
H. M.

3540. **A rapid method for the analysis of clinker and Portland cement.** G. N. Babachev. *Zhur. Anal., Khim.*, 1958, **13** (6), 716–718.—A rapid method is described for the determination of Si, Fe, Al, Ti, Ca, Mg, SO_4^{2-}, $CaSO_4$ and free CaO. Silica is separated and determined by the gelatin method; Al, after pptn. with aq. NH_3, as the fluoride; Fe, Ti, Ca and Mg complexometrically; SO_4^{2-} by igniting the sample at 1200° to 1300° and titrating the SO_3 liberated with iodine; $CaSO_4$ by passage of an aqueous extract of the sample through an ion-exchange column and titration of the eluate with NaOH soln., and free CaO complexometrically.
W. ROUBO

3541. **Identification of glass fragments by their physical properties.** J. Finch and P. P. Williams (Dominion Lab., D.S.I.R., Wellington, New Zealand). *Analyst*, 1958, **83**, 698–699.—Measurements have been made of the physical properties of glass fragments from 61 different objects, *viz*, bottles of various types, headlamp glasses, ophthalmic lenses and window plate-glass, all of which are often encountered in forensic work. Fluorescence was observed only with ophthalmic lenses. Among 100 ophthalmic lens blanks (including some bifocals), only one did not exhibit some fluorescence. In general, different colours were observed at the two exciting wavelengths (253·6 mμ and 300 to 400 mμ), and without exception the two parts of bifocals showed different fluorescence. Dispersion measurements had little significance. Ophthalmic lenses have a higher refractive index (1·5230 to 1·5242) than other glasses, but cannot be readily distinguished from one another. Bottles also tended to form a group, the range for 31 types of bottle being 1·5120 to 1·5170. Densities of ophthalmic lenses had a short range (2·5084 to 2·5184), but those of other types of object showed wide ranges, and wide ranges were found also with fragments from the same bottle. A. O. JONES

See also Abstracts—**3371**, Use of 2-(1-ethylpropyl)-8-hydroxyquinoline. **3372**, Colorimetric determination of Co, Pb and U. **3373**, Scheme of qual. analysis. **3376**, A new metal indicator. **3380**, EDTA titrations without metal indicators. **3381**, Indicators in complexometric titrations. **3382**, Use of tetraethylenepentamine for titration of metals. **3839**, Spectral analysis. **3846**, Determination of gases in metals. **3850**, Drop-scale chronopotentiometry. **3853**, Analysis of mixed γ-emitters.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives.

3542. **Paper chromatography of organic substances. II. Preparative micro-methods in paper chromatography.** V. Prey, A. Kabil and H. Berbalk (Inst. f. organ. Chem., Tech. Hochsch., Vienna). *Mikrochim. Acta*, 1959, (1), 68–78.—A microautoclave is described suitable for the preparation of derivatives of 100 to 500 μg of organic substances. The sample is transferred to glass-fibre 'paper' and the derivative is prepared and subsequently eluted in a special apparatus (described) and identified by normal paper chromatography. Details are given for the identification of alkyl halides as pyridine derivatives; of tertiary amines as methylammonium compounds; of hydrocarbons and aromatic halides as nitro derivatives; of primary and secondary alcohols as xanthates; and of carboxylic acids as hydroxamic acids. Results are quoted for 26 compounds.

III. Qualitative organic analysis by means of paper chromatography. V. Prey and A. Kabil. *Ibid.*, 1959, (1), 79–86.—The scheme described is suitable for the examination of 100 to 500 μg of organic mixtures; it is based on the separation of the several constituents into groups by simple chemical and chromatographic means, and the subsequent resolution of these groups by the methods described above. T. R. ANDREW

3543. **Quantitative organic micro-analysis below the milligram scale.** W. J. Kirsten (Inst. of Med. Chem., Univ. Uppsala, Sweden). *Microchem. J.*, 1958, **2** (2), 179–204.—Despite improvements in instrumentation in recent times, considerable difficulties in applying the new measuring methods to a simple 'scaling down' of the Pregl combustion procedures were encountered. For decimilligram and ultramicro analysis it has generally been necessary to design new methods for the destruction of samples and for the separation of elements. Available procedures are reviewed and in many cases commented on as a result of the author's practical experience. Suggestions for future workers and instrument manufacturers are offered. (121 references.) D. F. PHILLIPS

3544. **Elementary analysis using radiation sources.** J. S. Wiberley (Socony Mobil Oil Company Inc., Brooklyn, N.Y., U.S.A.). *Microchem. J.*, 1958, **2** (2), 219–227.—The replacement of combustion methods for C, H, O, N, Cl and S by radiation methods within ten years is predicted. A simple method depending on the absorption of X-rays from ^{55}Fe (half-life $\simeq$3 yr.) in petroleum samples is described. A limitation is that the content of C must be known to within 2% if S is to be correct to 0·1%. Beta-rays from ^{90}Sr may be applied to the determination of H. The moderation of fast neutrons produced by Ra - Be sources is suggested as a means of determining H, the principle already being used in commercially available instruments for the measurement of H present as H_2O in soils. Neutron-activation techniques coupled with the use of γ-ray spectrometers offer possibilities of simultaneous determination of several elements in organic compounds. It is suggested that the back-scatter of β-rays might assist the identification of an organic compound by comparing the percentage back-scatter of the sample with the calculated back-scatters of several possible formulae.

D. F. PHILLIPS

3545. **Determination of carbon and hydrogen in organic compounds containing phosphorus and sulphur. A rapid semi-micro method using silver permanganate.** I. Lysyj and J. E. Zarembo (Chem. Div., Food Machinery and Chemical Corp., Princeton, N.J., U.S.A.). *Microchem. J.*, 1958, **2** (2), 245–252.—The Körbl method (*Anal. Abstr.*, 1956, **3**, 733, 1384, 3067; 1957, **4**, 909, 910), in which the conversion of C into CO_2 and H into H_2O is accelerated by passing the products of combustion over thermally decomposed silver permanganate, is modified to provide good accuracy and precision in the analysis of organophosphorus and sulphur compounds. The silver permanganate packing is used without the asbestos buffer zone. A blast burner is used to heat the sample vigorously for 5 min. to effect complete combustion of phosphorus compounds. Oxides of S and P combine directly with silver wool and the central mass of decomposed silver permanganate. The special Körbl heating element used to prevent condensation of water in the capillary end of the anhydrone absorption tube is replaced by a simple steel hook which is connected to the stationary burner.

D. F. PHILLIPS

3546. **Organic micro-analysis. XVI. An investigation on the reaction product in a modified combustion tube for direct determination of oxygen.** Kazuo Imaeda (Pharm. Inst., Med. Fac., Kyoto Univ., Sakyo-ku, Kyoto). *J. Pharm. Soc. Japan*, 1958, **78** (1), 30–35.—The modified combustion tube containing I_2O_5 at the end (Kono, *J. Agric. Chem. Soc. Japan*, 1954, **28**, 581) and fitted with an absorber containing MnO_2 and $Na_2S_2O_3.5H_2O$ (Hozumi *et al.*, *J. Pharm. Soc. Japan*, 1956, **76**, 1161) is suitable for the analysis of acidic compounds containing halogen and S, but gives high results with compounds containing N. This is due to the formation of HCN, which produces CO_2 and H_2O on oxidation with I_2O_5. Attempts at the fractional combustion of CO and HCN were unsuccessful.

XVII. An improved method of determination of carbon monoxide by the Schütze method. Kazuo Imaeda. *Ibid.*, 1958, **78** (4), 386–391.—Instead of $Na_2S_2O_3.5H_2O$ for the absorption of iodine, silver powder, made by the following method, can be used—$AgNO_3$ (25 g in 500 ml of water) is treated with NaOH (6 g in 100 ml of water), the ppt. is washed with water (500 ml), dried at 150°, then heated at 500°, and the resulting silver is washed with 0·5% HNO_3 (100 ml) and water and dried at 150°. The CO is passed through a triple-walled cylinder containing, in the middle compartment, a lower layer of $\simeq$5 g of I_2O_5 and an upper layer of $\simeq$4 g of the Ag; the cylinder is heated from inside the central compartment by nichrome wire. The capture of iodine by the silver is quant. at 150°. The outlet gas (CO_2) is absorbed and weighed in the usual manner. This vertical cylinder can be attached to the combustion tube for the determination of N or of C and H. K. SAITO

3547. **Determination of nitrogen in certain fluorinated compounds.** T. R. F. W. Fennell and J. R. Webb (Royal Aircraft Estab., Farnborough, Hants, England). *Analyst*, 1958, **83**, 694–695.—The almost complete absence of reference to the Kjeldahl method in published methods for the determination of N in fluorinated compounds may give the impression that it cannot be used. A variety of solid fluorinated compounds have been successfully analysed by the Kjeldahl method. The procedure of Belcher and Godbert ("Semi-micro Quantitative Organic Analysis", 2nd Ed., Longmans, Green & Co. Ltd., London, 1954, p. 102) was used, but standard HCl was used instead of H_3BO_3 to receive the distillate. Examples show that no interference is caused by the presence of F, even in compounds containing nitro groups which were subjected to reduction with P and HI before digestion (Belcher and Godbert, *loc. cit.*).
A. O. JONES

3548. **Determination of phosphorus in organic compounds via flask combustion.** L. E. Cohen and F. W. Czech (Food Machinery and Chem. Corp., Westvaco Mineral Prod. Div., Carteret, N.J., U.S.A.). *Chemist Analyst*, 1958, **47** (4), 86–87.—Weigh solids (>2 mg of P) on to a holder of ashless filter-paper or liquids (>15 mg of sample) into a gelatin capsule which is wrapped in paper. Transfer the wrapped sample to the wire cage of a combustion flask containing 40 ml of *N* H_2SO_4. Flush the flask with O for 3 min. (5 min. with capsule), then ignite the paper tail of the wrapped sample, insert the stopper carrying the cage into the flask, and slowly invert it, shaking for 2 to 3 min. after combustion is complete. Make the contents of the flask up to 500 ml. Treat an aliquot (10 ml) with 8 *N* H_2SO_4 (8 ml) and water (22 ml) and boil slowly for 40 min. Cool, and dilute to 40 ml with water. Add 10% ammonium molybdate soln. (8 ml) and 50 ml of solvent mixture (equal vol. of *iso*butyl alcohol and thiophen-free benzene), and shake vigorously for 20 sec. Transfer 25 ml of the solvent layer to a 50-ml flask, add 15 ml of methanolic H_2SO_4 (20 ml of conc. acid diluted to 1 litre with methanol) and 1 ml of $SnCl_2$ soln. (0·2 g of $SnCl_2.H_2O$ in 0·5 ml of conc. HCl and 100 ml of *N* H_2SO_4; fresh daily). Mix, dilute to volume with methanolic H_2SO_4, set aside for 10 min., then read the colour in a 20-mm cell at 625 mμ, with a slit width of 0·065 mm, against a blank prepared with a filter-paper sample holder or wrapped gelatin capsule. Refer results to a calibration curve obtained with KH_2PO_4 soln. (5 μg of P_2O_5 per ml). Five analyses of tri-*p*-tolyl phosphate gave a mean of 8·32 ± 0·077% of P, the supplier's value being 8·34%. Analyses of 7 organic phosphorus compounds showed good agreement with the calculated value or that given by the supplier. Analyses should be completed soon after the combustion, as P_2O_5 may be lost from the soln. (about 5% in 24 hr.) probably owing to adsorption by the glass. R. E. ESSERY

3549. **Analytical procedure for compounds containing boron, carbon and hydrogen.** H. Allen, jun., and S. Tannenbaum (Lewis Res. Center, Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 265–268.—The organoboron compound is quant. oxidised with oxygen in an Inconel bomb at high temp. and pressure. The combustion products (CO_2, H_2O and hydrated boric oxide) are separated by conventional techniques and determined. The method was successfully applied to several trialkyl-borates and -boranes. For the C, H and B determinations, respectively, the precisions are ±0·11, ±0·07, and ±0·07% absolute, and the accuracies ±0·22, ±0·12 and ±0·1% absolute, in the ranges 60 to 88%, 11 to 16%, and 3 to 11% (approx. 30 analyses). G. P. COOK

3550. **Spectrophotometric studies for the synthesis of organostibonic acids. II. Colorimetric micro-determination of antimony in organic antimony compounds.** Yahyoe Kinoshita (Pharm. School, City Univ., Mizuho-ku, Nagoya). *J. Pharm. Soc. Japan*, 1958, **78** (4), 315–319.—Experimental conditions for the colorimetric determination of Sb with rhodamine B (C.I. Basic Violet 10) (**I**) were examined with reference to the application to the analysis of organostibonic acids. The decomposition of the sample is best effected by the use of conc. H_2SO_4 (2 ml) and K_2SO_4 (0·2 g) (for $\simeq$3 mg of Sb) followed by the addition of H_2O_2 (30%, 2 drops). For the extraction of Sb with di*iso*propyl ether, 6 *N* HCl is the optimum acid concn. in the presence of 0·02% of **I** (in *N* HCl, 2 ml).
K. SAITO

3551. **Review of methods employed for the detection, characterisation and assay of substances having a hydroxyl group (aliphatic, aromatic and heterocyclic).** S. Veibel (Univ., Copenhagen). *Parfum. Cosmét. Savons*, 1959, **2** (1), 2–8.—In this comprehensive review, the direct methods discussed include acetylation and bromimetric determination, and indirect methods include the preparation of xanthates, S-alkylthiuronium picrates, aryloxyacetates, *m*-nitrophenylcarbamates, *p*-nitrobenzoates and 3:5-dinitrobenzoates. H. B. HEATH

3552. **Semi-micro determination of the carbonyl group. Determination of phenylhydrazine and hydroxylamine.** B. Buděšínský (Res. Inst. Pharm. and Biochem., Prague). *Chem. Listy*, 1958, **52** (12), 2292–2295.—The reactions—

(*i*) $C_6H_5NH{\cdot}NH_2 + 2Cu^{2+} + 2OH^- = 2Cu^+ + C_6H_6 + N_2 + 2H_2O$,

and (*ii*) $2NH_2OH + 4Cu^{2+} + 4OH^- = N_2O + 4Cu^+ + 5H_2O$

have been applied to the potentiometric determination of phenylhydrazine (**I**) and hydroxylamine (**II**) with a pyridine - ethanolic soln. of Cu acetate, and to the indirect determination of the carbonyl group. The titration of 7 to 42 mg of **I** and 3·5 to 17·5 mg of **II** is carried out in a medium of 5 ml of pyridine with 1 ml of 0·05 *M* Cu acetate [dissolve 11 g of Cu acetate in 900 ml of ethanol - pyridine (1:1), set aside for 3 days, filter and determine the factor complexometrically or by titration of pure **I** hydrochloride; the factor changes after 3 days]. The average error is ±0·11% for **I** and ±0·46% for **II**. 2:4-Dinitrophenylhydrazine can also be determined by this method. *Procedure for carbonyl groups*—Dissolve 0·15 to 0·20 milli-equiv. of the sample in pyridine and add 38 to 40 mg of **I** hydrochloride. Remove air from the reaction mixture with a stream of N, close the flask and heat on a water bath for 15 min.; cool and titrate potentiometrically in a stream of N with 0·05 *M* Cu acetate. The suitability of the procedure has been tested with good results by the determination of the carbonyl group in acetone, ethyl methyl ketone, methyl propyl ketone, benzaldehyde, isatin, and ethyl phenylglyoxylate. J. ZÝKA

3553. **Determination of carbonyl compounds.** J. S. Fritz, S. S. Yamamura and E. C. Bradford (Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 260–263.—The compound is oximated in methanol - *iso*propyl alcohol and the excess of hydroxylamine is titrated with standard $HClO_4$ to a potentiometric or visual end-point, with Martius yellow (C.I. Acid Yellow 24) as indicator. Recoveries from 4 compounds of known purity were >99%. The assay of 15 compounds gave results generally >98%, with an average deviation from the mean of ±0·2%. G. P. COOK

3554. **Determination of the carbamoyl grouping in non-aqueous medium.** O. Cerri, A. Spialtini and U. Gallo (Ist. Sieroterapico Milanese "S. Belfanti," Milan, Italy). *Pharm. Acta Helv.*, 1959, **34** (1), 13–18 (in French).—The method is applicable to carbamates in which there is no N-substitution. Amides, urea, thiourea, semicarbazones and biuret cause no interference. *Procedure*—Dissolve the sample (1 or 2 milli-equiv.) in pyridine (10 ml) and heat under reflux with a 0·1 *N* soln. of Na methoxide in benzene - methanol (17:3) (25 ml) for 1 hr. with exclusion of moisture. Cool and titrate with a 0·1 *N* soln. of benzoic acid in benzene, with thymol blue as indicator. Perform a blank titration. Alternatively, weigh the sodium cyanate which is pptd. during the ebullition with alkali.
A. R. ROGERS

3555. **Organic micro-analysis. III. Micro-determination of the methoxyl group.** Minoru Fukuda and Tatsuei Sai (Pharm. Fac., Osaka Univ., Hotarugaike, Toyonaka). *J. Pharm. Soc. Japan*, 1958, **78** (1), 101–102.—In place of N or CO_2, air can be used in the distillation of alkyl iodide, following the decomposition of the methoxyl or ethoxyl group (*e.g.*, Neuman's procedure, *Ber.*, 1937, **70**, 734). Iodine is not distilled.

IV. A new micro-determination of methoxyl and ethoxyl groups by a combustion method. Minoru Fukuda and Tatsuei Sai. *Ibid.*, 1958, **78** (1), 83–86.—The vapour of the distillate obtained by the above-mentioned procedure is introduced, via an air-cooled reflux condenser, into a combustion tube containing a platinum catalyst, and the liberated iodine is absorbed by rolled silver gauze for subsequent gravimetric determination. Iodine is instantaneously captured at >150° (30 minutes' flow, at a rate of <20 ml per min.). The sample (3 mg) is dissolved in a mixture of phenol and propionic acid (4:1, by wt.) (0·5 ml) and boiled with HI (sp. gr. 1·7, previously distilled over red phosphorus) (2 ml) in a current of air (10 ml per min.) for 30 min.
K. SAITO

3556. **Gas-chromatographic micro-determination of formyl and acetyl groups, particularly in digitalis glycosides.** H. Spingler and F. Markert (Forschungslab. der Fa. C. F. Boehringer u. Söhne, Mannheim-Waldhof). *Mikrochim. Acta*, 1959, (1), 122–128.—A sample (0·005 to 0·02 milli-equiv.) is heated with 20 mg of toluene-*p*-sulphonic acid and 300 µl of methanol for 30 min. in an oil bath at 70° to 80°. The distillate is collected in a graduated receiver cooled to −10° by an ice - salt mixture. The vol. of distillate is recorded and a 20-µl aliquot is transferred to a Perkin-Elmer 'Fractometer' 154 B. Gas chromatography is carried out, with helium as carrier gas. Good results are reported for 13 substances (errors −0·95% to +0·45% absolute).
T. R. ANDREW

3557. **Experiments in the analysis of the acid functional group. Conclusion.** E. A. M. F. Dahmen (Koninklijke/Shell Lab. Amsterdam, Holland). *Chim. Anal.*, 1958, **40** (11), 430–434.—A review of suitable methods of determining carboxylic acids is concluded. The determination of formic acid, in the presence of acetic acid, by oxidation with Pb tetra-acetate, and analysis by azeotropic distillation with $CHCl_3$ are discussed. For small quantities of acetic acid in the presence of formic acid the mass spectrometer is preferred, and the distribution of intensities in the various mass peaks for 9 acids is given. For several acids, gas chromatography is the preferred method and is described.
E. J. H. BIRCH

3558. **Titanous chloride as a reagent for quantitative organic micro-analysis. I. Micro-determination of nitro and nitroso groups.** T. S. Ma and J. V. Earley (Dept. of Chem., Brooklyn Coll., N.Y., U.S.A.). *Mikrochim. Acta*, 1959, (1), 129–140 (in English).—Titanous chloride soln. (0·04 *N*) has been stabilised by adding 100 ml of 12 *N* HCl and 200 g of amalgamated zinc per litre and preventing photo-oxidation by wrapping the storage vessel with aluminium foil. To determine nitro compounds, weigh 3 to 8 mg into a modified Erlenmeyer flask (illustrated) containing 4 ml of ethanol (95%), stir until dissolved, attach to a modified Machlett micro-burette, add 7 ml of 2·5 *M* Na acetate and flush with *N* at 20 ml per min. for 5 min. Titrate with 0·04 *N* $TiCl_3$ until the soln. is deep violet and set aside for 3 min. Add 4 ml of 12 *N* HCl and connect to a 5-ml micro-burette. Titrate with 0·035 *N* $(NH_4)_2SO_4.Fe_2(SO_4)_3$ until the blue colour is almost discharged, add 2 ml of 2·5 *M* NH_4SCN and continue the titration until a pink colour,

stable for 1 min., is obtained. The procedure is modified slightly for nitroso compounds: 4 to 9 mg is dissolved in 5 to 10 ml of water or ethanol, 5 ml of 2·5 *M* Na acetate is added, and 0·03 *N* $TiCl_3$ and 0·025 *N* $(NH_4)_2SO_4.Fe_2(SO_4)_3$ used for titration. N-Nitroso compounds must be allowed to stand for 10 min. with a 50 to 150% excess of $TiCl_3$ before adding HCl. Nineteen nitro and 10 nitroso compounds have been studied and good results (±0·5% relative error) reported, except for aliphatic nitro compounds and aromatic compounds having the nitro group in a side-chain. Cupferron gave high results owing to cleavage of the N–N bond. C-Nitroso compounds (not N-nitroso) may be determined in the presence of some nitro compounds by replacing the Na acetate soln. by 12 *N* HCl.

T. R. ANDREW

3559. **Identification and determination of O- and N-benzylidene groups.** M. Jureček and K. Obruba (Inst. Anal. Chem., High-School of Chem. Technol., Pardubice, Czechoslovakia). *Chem. Listy*, 1958, **52** (11), 2066–2072.—The semi-micro- and micro-method described is based on the fission of the benzylidene groups by acid hydrolysis, and distillation of the benzaldehyde so produced into a known excess of 4-nitrophenylhydrazine (**I**) or 2:4-dinitrophenylhydrazine (**II**) soln., the excess of which, after the separation of the hydrazone, can be determined volumetrically with Ti^{3+}. *Procedure*—Place the sample (10 to 15 mg if using **II**; 20 to 25 mg if using **I**; 4 to 6 mg for the micro-determination with **II**) into a distillation apparatus modified according to Kuhn and Roth (*Ber.*, 1933, **66**, 1274), add H_2SO_4 (60%) (5 ml), heat for 30 to 40 min. at 135° to 140°, distil the benzaldehyde with H_2O into an absorption vessel containing 0·01 *M* **II** (10 ml) or 0·02 *M* **I** (10 ml). Set aside for 1 hr. (with **II**) or 6 to 8 hr. (with **I**). Filter off the ppt. and wash 5 to 6 times with 2 *N* HCl (30 ml with **II**, 20 ml with **I**, or 10 ml in the micro-determination); add to the filtrate 2 ml of a mixture of conc. HCl and 40% HF (13:1), remove O by bubbling for 5 min. with N, add 0·4 *N* $TiCl_3$, boil for 30 min. in an atmosphere of N, cool, add NH_4SCN soln. as indicator and titrate with 0·1 *N* $(NH_4)_2SO_4.Fe_2(SO_4)_3$ till pink. Benzylidene diacetate, tribenzylidene mannitol, benzylidine-*o*-aminophenol, benzylidene-*m*-nitroaniline, dibenzylidenebenzidine, dibenzylidene-*p*-phenylenediamine, benzaldehyde 2:4-dinitrophenylhydrazone and benzaldehyde semicarbazone have been determined by this procedure, and good results were obtained. **II** is preferred as reagent on account of the lower solubility of the hydrazone.

J. ZÝKA

3560. **Rapid photometric determination of phosphine in acetylene.** Fumikazu Kawamura and Hiroshi Namiki (Fac. of Engng, Yokohama Univ., Minami-ku). *Japan Analyst*, 1958, **7** (11), 691–695.—The absorption of PH_3 in 0·3% aq. bromine soln. proceeds rapidly; the excess of Br is reduced with Na_2SO_3, and neither Br^- nor Na_2SO_3 interferes with the colorimetric determination of P by the molybdenum blue method. The amount of PH_3 in acetylene differs appreciably according to the conditions under which CaC_2 reacts. The time taken for an analysis is 15 min. *Procedure*—Collect the sample (50 ml) in a syringe and inject the gas into 0·3% aq. bromine soln. (20 ml) within 1 min. Add Na_2SO_3 soln. (10%) until the soln. becomes colourless. Dilute the product to 50 ml after the addition of ammonium molybdate soln. (1·5% in 6·5 *N* H_2SO_4) (5 ml) and $SnCl_2$ (2% in *N* HCl) (0·25 ml), set aside at 25° for 10 min. and determine the P colorimetrically.

K. SAITO

3561. **Determination of 1:2-dibromoethane in brine.** J. R. Marshall and D. A. Ader (Israel Mining Ind. Lab., Haifa). *Analyst*, 1958, **83**, 687–688.—The method was developed for the determination of 1:2-dibromoethane (**I**) in brine obtained during the manufacture of **I**. The brine, containing 10 to 200 mg of **I**, is extracted three times with xylene (4 to 5 ml). The separated extract is washed free from Cl^- and is then heated under reflux with KOH (4 to 5 g) and *n*-butanol (a solvent for KOH and xylene) in a bath of saturated NaCl soln. for 1 hr. The digest is diluted, neutralised with dil. HNO_3, slightly acidified with the same acid, and Br^- are pptd. as AgBr. The collected ppt. is washed with water to remove $AgNO_3$ and with *iso*propyl alcohol to remove xylene, dried at 120° to 130°, and weighed, and the weight is corrected for a reagent blank. If the brine sample contains free halogen, this is converted into halide by addition of excess of KI and titration of the liberated iodine with $Na_2S_2O_3$ soln. before extraction of the sample with xylene. Quoted results with samples of known **I** content indicate an accuracy within ±1%.

A. O. JONES

3562. **Determination of alcohols by oxidation.** P. Jaulmes and R. Mestres (Fac. de Pharm., Montpellier, France). *Chim. Anal.*, 1958, **40** (11), 413–424.—After a review of oxidative methods of determining alcohols, a standard procedure is described, based on the method of Semichon and Flanzy (*Ann. Falsif.*, 1929, **139**, 414). The oxidising soln. is 0·276 *N* with respect to $K_2Cr_2O_7$ and 7 *N* with respect to H_2SO_4 (20% v/v). After various times of oxidation the excess of $K_2Cr_2O_7$ is determined by titration with Fe^{2+}, with ferrous 1:10-phenanthroline as indicator, correcting any slight excess at the end-point by back-titrating with $KMnO_4$ soln. Volatile acids formed are determined after steam-distillation. Ethanol can be quant. determined, since oxidation to acetic acid is complete in 30 min. and the acetic acid is not attacked except under more drastic conditions. It is suggested that this chemical method could be used to standardise the various tables of 'alcoholic degrees' which vary from country to country. With methanol, the formic acid produced is oxidised under the standard conditions and the only possible method of analysis is to oxidise completely to CO_2 and H_2O, requiring 12 hr. A mixture of methanol and ethanol may be determined by a 12-hr. oxidation (total alcohol) followed by determination of the volatile acid produced (acetic acid from the ethanol only). Oxidations of higher primary alcohols are described under the standard conditions and more and less rigorous ones, and in all cases acids with fewer C atoms than the alcohol are produced in addition to the expected acid. Under the standard conditions these alcohols consume 2·45 to 2·8 (usually 2·75) atoms of O per mol. in 24 hr. The nature of the alcohol can be qual. determined by paper chromatography of the acids liberated. *iso*Propyl alcohol is oxidised quant. to acetone in 15 min. by the standard oxidant, and the acetone is not oxidised in 8 days. (With 47·7% H_2SO_4 the acetone is oxidised in 4 days to acetic acid which is itself considerably oxidised.) *sec.*-Butyl alcohol is oxidised slowly but quant. to acetic acid (3 atoms of O per mol. in 3 months). Oxidation of tertiary alcohols is very slow. Allyl alcohol is quant.

oxidised very rapidly, consuming 8 atoms of O per mol. and forming CO_2 and H_2O. Benzyl alcohol is quant. oxidised in 5 to 6 hr. to benzoic acid, which remains unoxidised under the standard conditions for 8 days. Lactic acid consumes 2 atoms of O per mol. in 4 hr. and is not further oxidised in 16 months. E. J. H. BIRCH

3563. **Chromatography of alcohols and phenols. Methods of isolation and characterisation of alcohols.** B. Gastambide. *Parfum. Cosmét. Savons*, 1958, **1** (11), 423–427.—Conditions influencing the adsorption of the hydroxyl group in partition chromatography are discussed. Methods of obtaining primary and secondary alcohols in an aqueous phase are reviewed. The preparation of malonates by reaction with malonyl chloride is described, the melting-points of the derivatives being used as a means of identification. H. B. HEATH

3564. **Determination of *tert.*-butyl alcohol and acetone concentrations in the products of isobutane oxidation by infra-red absorption spectra.** G. B. Meluzova and A. A. Babaeva (M.V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1958, **13** (6), 706–708.—A trap, immersed in liquid nitrogen, is used to freeze the gaseous products of the reaction. Exactly 2 ml of CCl_4 as solvent is introduced into the trap and measurements are carried out at 1718 and 918 cm^{-1}. The extinction coefficient K for 1718 cm^{-1} for acetone is 300 mol^{-1} l/cm^{-1} at the spectral width of the slit of 12 cm^{-1} and this coefficient for 918 cm^{-1} for *tert.*-butyl alcohol is $K = 90$ mol^{-1} l/cm^{-1} at the spectral width of the slit of 6 cm^{-1}. Apparatus corrections are not required. Results are accurate to within ±3%. W. ROUBO

3565. **Micro-determination of glycerol in *Acetobacter* culture media.** C. P. Jackson and K. Ramamurti (Chem. Dept., Div. of Ind. Biochem., Manchester Coll. of Sci. and Technol., England). *J. Sci. Food Agric.*, 1958, **9** (12), 787–791.—Metabolites from glycerol attacked by *Acetobacter acetigenum* are destroyed by oxidation with $Ce(SO_4)_2$ and hypoiodite and the residual glycerol is determined colorimetrically. *Procedure*—Heat a 2-ml sample (0·1 to 0·5 mg of glycerol) with 1·2 ml of 10 *N* H_2SO_4 and 2 ml of 0·01 *N* $Ce(SO_4)_2$ at 100° for 5 min.; precipitate the excess of Ce^{4+} with NaOH and centrifuge. Decant the supernatant liquid, wash the residue twice and combine the supernatant liquids (total vol. 20 ml). Add 4 drops of 0·1 *N* iodine, set aside in darkness for 10 min. and add 2 ml of 10 *N* H_2SO_4. Add 5 ml of 0·1 *M* HIO_4 and, 5 min. later, 5 ml of *M* Na_2AsO_3; 10 min. after decolorisation of the iodine, dilute to 100 ml and treat 1 ml with 10 ml of 0·2% chromotropic acid in 10 *N* H_2SO_4 at 100° for 30 min. Cool and measure the extinction at 580 mμ; 0·1 to 0·5 mg of glycerol can be determined in the presence of 0·76 mg of dihydroxyacetone. The precision is related to the accuracy of prediction of the amounts of glycerol in unknown soln. from standard curves prepared with aq. glycerol soln.; 95% confidence limits over the determinative range from 0·1 to 0·5 mg of glycerol are ±0·01 mg to ±0·011 mg. The limitations of the method are discussed. P. D. PARR-RICHARD

3566. **Paper-chromatographic analysis of carbohydrates.** F. Schneider and A. Emmerich (Inst. f. Landwirtschaft. Technol. u. Zuckerindust., Tech. Hochsch., Braunschweig). *Stärke*, 1959, **11** (1), 1–7.—This concise review describes also the use of the double salt of dimethyl-*p*-phenylenediamine hydrochloride and $SnCl_2$ as a universal reagent for the detection of reducing and non-reducing sugars and similar substances. On a pink background aldoses appear as yellow-brown spots, ketoses carmine, and pentoses strong red. Oligosaccharides are hydrolysed by the acid reagent and appear as a mixture of the colours given by their components. The reagent is sensitive to 3 μg but can be improved to detect 1 μg by using u.v. light. The best solvents are *n*-butanol - acetic acid - water (4:1:5) and *n*-propanol - ethyl acetate - water (7:1:2). Explanations are given of the de Bruyn - van Ekenstein transformation and the formation of oligomers arising from glucose and fructose when heated in alkaline, acid or neutral media.

E. DUX

3567. **Qualitative test for aldehyde in acetone.** M. Zeman, M. Klátil and K. Pánek (Chem. Lab. Svit n.p., Gottwaldov, Czechoslovakia). *Chem. Prûmysl*, 1958, **8** (12), 638–639.—Schiff's and Tollens' reagents have been studied for the reliability of their use for the detection of aldehydes in commercial acetone. It is concluded that these reagents are unsuitable for this purpose, because a positive reaction has been obtained even with chemically pure or specially purified specimens of acetone. No difference has been observed when testing purified and technical samples of acetone by these methods. It is concluded that for such cases the Schiff's and Tollens' reactions are unreliable and that the polarographic method is preferable. J. ZÝKA

3568. **Simple spot test for methyl ketones.** T. W. Stanley (Taft Engng Center, U.S. Dept. of Health, Education and Welfare, Cincinnati, Ohio). *Chemist Analyst*, 1958, **47** (4), 91.—Replacing $(NH_4)_2SO_4$ with ammonium acetate in the nitroprusside test for acetone bodies, renders the test more sensitive and specific than the older versions; it can be carried out in methanol soln., and is applicable to compounds insol. in water. The reagent (3 parts of sodium nitroprusside, 50 parts of ammonium acetate and 50 parts of anhyd. Na_2CO_3, ground to a uniform powder) is satisfactory if stored in a tightly stoppered bottle and used within 24 hr. For the test, overlay 50 mg of reagent with 0·1 ml of a methanolic soln. of the suspected compound, set aside for 10 to 30 min., and note the colour. For the determination of wavelength maximum, overlay 50 mg of reagent with 1 ml of methanol containing 1 mg of compound, allow the colour to develop and examine the absorption between 525 and 640 mμ. Colours (purple, blue or green), wavelengths of max. absorption and detection limits (usually 1 to 5 μg) are listed for 20 compounds that give a positive reaction, and a further 12 compounds that do not respond to the test are named. R. E. ESSERY

3569. **Chromatography of organic compounds. I. Separation of thiosemicarbazones of aliphatic ketones by paper chromatography.** J. Franc (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1958, **52** (12), 2311–2315.—The chromatography was carried out by the descending technique on Whatman paper No. 1, impregnated with a 30% ethanolic soln. of formamide or dimethylformamide, or with a 20% soln. of acetamide. Aliquots (2 to 10 μg) of the thiosemicarbazone dissolved in ether were placed on the paper and developed with various solvent systems [CCl_4, chlorobenzene, chloro*cyclo*hexane,

and *cyclo*hexane - *n*-butanol (25:1)] at 26° to 31°. For the detection, the chromatogram was moistened with 5% $AgNO_3$ soln. and passed through 1 to 2% aq. NH_3 soln. (black spots). As little as 1 to 2 μg of a thiosemicarbazone can thus be detected; the detection can also be made with a 1% soln. of *p*-dimethylaminobenzaldehyde (**I**) in 2 *N* HCl (yellow spots, blue or orange in u.v. light). Thiosemicarbazones were prepared by heating 1 ml of ketone and 1 g of thiosemicarbazide (**II**) under reflux on a water bath for 1 hr., cooling and extracting with diethyl ether. *Determination of methylcyclohexanone* (**III**) *in technical cyclohexanone*—Dissolve **I** (1 g) in H_2O (25 ml) with heating, add the sample (1 ml) dissolved in ethanol (2 to 3 ml) and heat for 5 to 10 min. Filter off the crystals on a glass filter (G3), wash with H_2O, dissolve in ethanol and separate chromatographically on Whatman paper impregnated with 25% formamide soln., with *cyclo*hexane - *n*-butanol (25:1) as solvent. For the semi-quant. evaluation, a comparison scale (0·25 to 1% content of **III**) was prepared. *Determination of* p-*tolualdehyde in technical dimethyl terephthalate*—Heat the sample (1 g) with **II** (1 g) and ethanol (3 ml) for 1 hr. under reflux. Extract with diethyl ether and evaporate to 5 ml. Treat 0·25 ml of the extract chromatographically as described above, detect the spots with **I** and compare with a soln. of a standard. R_F values are given for 17 compounds. Some theoretical relations are discussed. J. ZÝKA

3570. **Gas - liquid chromatographic analysis of some oxygenated products of cool-flame combustion.** G. Kyryacos, H. R. Menapace and C. E. Boord (Ohio State Univ., Columbus, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 222–225.—Hitherto unidentifiable compounds recognised include ethylene oxide, propionaldehyde, acetone, acraldehyde, tetrahydro-*trans*- and -*cis*-2:5-dimethylfuran, *n*-butyraldehyde, ethyl methyl ketone, methyl vinyl ketone, 2-ethyltetrahydrofuran, methanol and crotonaldehyde. Identification was assisted by means of i.r. spectrophotometry. G. P. COOK

3571. **Paper chromatography of saturated aliphatic monocarboxylic acids.** F. Baykut and S. Baykut. *Rev. Fac. Sci. Univ. İstanbul, Ser. C*22, 1957, 267–270 (in German).—A simple mathematical relationship was worked out between the R_F value and the number of C atoms in the homologous series of higher aliphatic saturated monocarboxylic acids from C_{16} to C_{22}. Light petroleum (boiling-range 190° to 200°) was used as the stationary phase, and light petroleum saturated with a 90% acetic acid - water mixture as the mobile phase. Strips of special paper (40 cm × 14 cm) were hung from a balance under a hood. Light petroleum was first injected on to the paper and the fatty acid, in $CHCl_3$ soln., was applied at the starting point. The paper was allowed to stand for 24 hr. at 25° ± 0·1°. The mobile phase was then applied and allowed to act for 8 to 20 hr. The papers were dried at 110° and then placed in a Cu acetate soln. Insol. copper salts of the fatty acids were formed. The excess of Cu acetate was washed away with water containing 2 ml of acetic acid. The chromatogram was then dipped in 2% $K_4Fe(CN)_6$ soln. for 5 min. The fatty acids were then revealed as brown spots. A table is given showing the number of C atoms of the acids and the corresponding R_F values. A graph is also plotted for this relationship. From this an equation is given, $R_F = 1{\cdot}671 - 0{\cdot}1326n + 0{\cdot}0028n^2$, where n is the number of C atoms in the fatty acid.

CHEM. ABSTR.

3572. **Thermometric titration of weak monoprotic acids.** J. Jordan and W. H. Dumbaugh, jun. (Pennsylvania State Univ., University Park, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 210–213.—Four acids, whose ionisation constants covered a range of 9 orders of magnitude, were studied at concn. of 10^{-3} to 10^{-1} *M*. Kinetic effects were eliminated by using an automatic procedure which maintained the rate of addition of the titrant (NaOH) to one millionth of the prevailing rates of neutralisation. The end-points were precise and accurate to ±1% for concn. $< 3 \times 10^{-3}$ *M*. Within the range studied, ionisation constants had no effect on the precision and accuracy because the heats of neutralisation were approx. equal. The experimental method was that of Jordan and Alleman (*Anal. Chem.*, 1957, **29**, 9). G. P. COOK

3573. **Control methods in lactic acid production. V. Improvement of accuracy in the determination of lactic acid.** A. Šepitka (Dept. of Carbohydrates and Biochem., Chem. Inst. Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1958, **12** (12), 699–702.—A method for the calculation of the purity of lactic acid from its concn. and density at 20° by means of a table of densities at various concn. of pure lactic acid is described. J. ZÝKA

3574. **Quantitative determination of glyoxylic acid.** D. N. Kramer, N. Klein and R. A. Baselice (Army Chem. Center., Md., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 250–252.—The method is based on the formation of the intensely coloured 1:5-diphenylformazancarboxylic acid, obtained by the mild oxidation of glyoxylic acid phenylhydrazone in the presence of phenylhydrazine. Beer's law is obeyed at 520 mμ in the concn. range 10^{-4} to 10^{-6} *M*. The precision is ±5%. With suitable modifications the method may be used as a general procedure for aldehydes. Alcohols, ketones, acids and esters, excepting formates, do not interfere.

G. P. COOK

3575. **Spot-test detection of N-cyano compounds.** F. Feigl and V. Gentil (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Mikrochim. Acta*, 1959, (1), 44–45 (in English).—The solid or a drop of its soln. is heated in a small test-tube with a few zinc granules and several drops of HCl (1:5). The mouth of the tube is covered with a reagent paper and the tube immersed in boiling water. A blue colour indicates the presence of an N-cyano compound. The reagent paper is prepared just before use by impregnating filter-paper with a fresh soln. made by mixing equal vol. of (*a*) 0·286% aq. Cu^{II} acetate soln. and (*b*) 675 ml of satd. aq. benzidine acetate soln. diluted with 525 ml of water. Approx. 10 μg of N-cyano compound may be detected in one drop. T. R. ANDREW

3576. **Spot test for aliphatic and aromatic cyanides.** F. Feigl, V. Gentil and E. Jungreis (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Mikrochim. Acta*, 1959, (1), 47–50 (in English).—Aliphatic and aromatic cyanides evolve HSCN when heated in the presence of sulphur. Mix the sample with 10 mg of sulphur in a micro test-tube, cover the mouth of the tube with a filter-paper impregnated with acidified $FeCl_3$ soln. (1%), and heat, starting at the upper portion of the tube and moving

downwards. A red spot is given by 1 to 20 μg of cyanides. Compounds containing C=N groups interfere and must be separated. Aliphatic cyanides give off HCN when heated in the presence of CaO and $CaCO_3$. The sample is mixed with a few mg of CaO - $CaCO_3$ mixture (1:1) in a micro test-tube, the mouth is covered with Cu^{II} acetate - benzidine acetate paper, and the tube is heated in a glycerol bath at 250°. A blue stain is given by 2 to 50 μg of aliphatic cyanide. This test is specific for aliphatic cyanides. T. R. ANDREW

3577. **Polarographic determination of nitriles.** M. I. Bobrova and A. N. Matveeva-Kudasheva (Leningrad. Inzhenerno-Ekonomichesk. Inst.). *Zhur. Obshch. Khim.*, 1958, **28** (11), 2929–2932.—The work previously reported (*cf. Anal. Abstr.*, 1958, **5**, 567) is continued. The basal soln. are 0·14 *N* LiCl in 50% or 75% ethanol. Cinnamonitrile (in 75% ethanol) has a $E_{\frac{1}{2}}$ of −1·95 V; α-phenylcinnamonitrile (**I**) has a $E_{\frac{1}{2}}$ of −1·85 V (in 75% ethanol) and of −1·94 V (in 50% ethanol); fumaronitrile (**II**) (in 50% ethanol) has two waves with $E_{\frac{1}{2}}$ of −1·30 and −2·2 V; and αα′-azoisobutyronitrile (**III**) (in 50% ethanol) has a $E_{\frac{1}{2}}$ of −1·80 V. In all cases the value of the limiting diffusion current is directly proportional to the concn. of the nitrile. The number of electrons transferred per molecule of nitrile are 0·48, 0·92, 0·64, 0·32 (first stage) and 0·38 (second stage), and 0·35, respectively, these fractional values indicating the irreversible nature of the polarographic reduction. When polarographing mixtures of **I**, **II** and **III**, the resulting polarograms have diffusion waves corresponding to the reduction of each component. C. D. KOPKIN

3578. **Solubility of ethylenediaminetetra-acetic acid (Complexone II) as a function of pH.** P. Mechelynck and W. Schietecatte (Section de Chim. Anal., Centre d'Étude de l'Énergie Nucléaire, Mol, Belgium). *Anal. Chim. Acta*, 1958, **19** (6), 577–579 (in French).—The solubility of EDTA in soln. of pH 1·13 to 7·3 has been determined by amperometric titration of satd. soln. with standard Zn^{2+} soln. The solubility reaches a minimum of $1·73 \times 10^{-4}$ *M* at pH 2 and rises to about 2 *M* at pH 4·6 to 7·3. T. R. ANDREW

3579. **Micro-determination of maleic hydrazide by reductive cleavage with zinc in sulphuric acid.** Yasutoyo Nagai (Fac. of Agric., Tokyo Univ., Hongo). *J. Agric. Chem. Soc. Japan*, 1958, **32** (11), 851–855.—Maleic hydrazide (**I**) produces hydrazine quant. when heated with zinc in *N* H_2SO_4. The product is determined colorimetrically with *p*-dimethylaminobenzaldehyde (**II**) (*cf.* Wood *Anal. Abstr.*, 1954, **1**, 1125). This method is much simpler than that involving the decomposition of **I** with zinc in NaOH. Ascorbic acid and fructose interfere. *Procedure*—Heat the sample soln. (1 ml) with 8 *N* H_2SO_4 (1 ml) and zinc dust (300 mg) at 110° for 2 hr. Add **II** (2% in 2 *N* H_2SO_4, 1 ml) and water (8 ml) and measure the extinction at 300 mμ after 30 min. K. SAITO

3580. **Determination of maleic hydrazide. III. Conductimetric titration.** Shigeru Shimomura (Fac. Pharm., Tokushima Univ., Sho-machi). *J. Pharm. Soc. Japan*, 1958, **78** (6), 589–593.—The effect of impurities, including hydrazine (**I**), maleic acid (**II**) and N-aminomaleimide (**III**), upon the conductimetric titration of maleic hydrazide (**IV**) with *N* NaOH was examined. There is no interference from **I** and diethylamine (solvent for commercial products). A half-equiv. of **II** and **III** reacts with NaOH, but the slope of the graph of conductance *vs.* vol. of NaOH soln. is different from that for **IV**, two inflection points being observed for **IV** containing **II** and **III**. The amount of NaOH required to reach the first inflection point corresponds to that consumed by **II** and **III**. This amount is subtracted from the amount of NaOH consumed between the two inflection points, and the purity of **IV** calculated. To make the first inflection point sharper, the addition of a known amount of H_2SO_4 (0·1 *N*) is recommended. K. SAITO

3581. **Determination of dimethylurea in the presence of methylurea.** F. Jančik, B. Kakáč and V. Vaníček (Res. Inst. of Pharm. and Biochem., Prague). *Chem. Listy*, 1958, **52** (11), 2181–2183.—Methylurea (**I**) reacts with *p*-dimethylaminobenzaldehyde (**II**) to give a yellow coloration. NN′-Dimethylurea does not interfere. *Procedure*—Dissolve the sample (containing 0·2 to 0·3 mg of **I**) in a 25-ml flask in a little twice-distilled H_2O, add the reagent (2 g of **II** dissolved in 100 ml of 95% ethanol and 20 ml of conc. HCl) (10 ml), dilute with H_2O to vol. and measure the extinction after 10 min., with violet filter No. 601 ($E_{max.}$ = 420 to 425 mμ). The colour is stable for 6 hr. Refer the results to a calibration curve. Beer's law is obeyed between 0·2 and 1·6 mg of **I** in 25 ml. The average error is ±1·21%. Compounds with primary amino groups interfere. A method for the analysis of binary mixtures of **I** with NN′-dimethylurea, based on determination of the freezing-point, is also described. If wet samples are being analysed, a correction, determined by means of the Karl Fischer method, must be applied. J. ZÝKA

3582. **Ultra-violet photometric micro-determination of biuret as the manganese complex.** Yasuto Watanabe (Fac. of Agric., Kyushu Univ., Hakozaki, Fukuoka). *J. Agric. Chem. Soc. Japan*, 1958, **32** (11), 842–847.—The u.v. absorption of the complexes of biuret with various metal ions was examined and it was found that Mn^{2+} gave a distinctive strong absorption at 223 mμ; the extinction is proportional to the concn. of biuret for 0·1 to 1 mg per 10 ml in 0·8 *N* NaOH. In this soln. excess of Mn^{2+} is pptd. as hydroxide. Biuret is separated by paper chromatography with *n*-butanol satd. with water, the spot is cut out, and immersed in an aq. soln. (10 ml) containing 2 *N* NaOH (4 ml) and $MnSO_4$ (10 mg per 100 ml) (2 ml) for 10 min., then centrifuged at 3000 r.p.m. for 10 min. The supernatant liquid is measured photometrically. K. SAITO

3583. **Reactions of amides with formaldehyde. XI. The determination of bound formaldehyde in urea - formaldehyde condensation products.** R. Květoň (Sběrné Suroviny, Střelské Hoštice, Czechoslovakia). *Chem. Listy*, 1958, **52** (11), 2178–2180.—The behaviour of urea - formaldehyde condensation products in alkaline and acid media is said to depend on the character of the substituents on the urea nitrogen. CH_2OH groups in the presence of CH_2 and OCH_2O groups can be determined iodimetrically (de Jong and de Jong, *Rec. Trav. Chim. Pays-Bas*, 1952, **71**, 643) when sol. condensates are being analysed. For insol. condensates the cyanide method is preferred (*cf.* de Jong, *Brit. Abstr. C*, 1953, 509). J. ZÝKA

3584. **Scheme for the colorimetric determination of microgram amounts of thiols.** B. Saville (Chem. Defence Expt. Estab., Porton Down, Salisbury, Wilts., England). *Analyst*, 1958, **83**, 670–672.—The thiol soln. (1 ml) in water or aq. ethanol is added to 5 ml of HNO_2 soln. ($NaNO_2$ - dil. H_2SO_4) and after 0·5 to 5 min., according to the nature of the thiol, 1 ml of a 0·5% aq. soln. of ammonium sulphamate is added to remove the excess of HNO_2, and the liquid is well shaken. The S-nitrosothiol formed is hydrolysed and a diazonium salt is formed by the addition of a soln. of sulphanilamide and $HgCl_2$ in dil. HCl and finally a freshly prepared soln. of N-1-naphthylethylenediamine dihydrochloride in HCl is added. When colour development is complete the vol. is adjusted, and the colour is measured against an appropriate blank in a Spekker absorptiometer with Ilford No. 605 filters. The accuracy depends on the concn. of the thiol soln., and ranges from ±10% for 1 ml of 0·00002 *M* thiol to ±1 to 2% for 0·00004 *M* soln. Owing to the relative rapidity of the reaction, interference from small amounts of such compounds as dialkylamines is negligible. As the rate of S-nitrosation of cysteine is much greater than the rate of de-amination of simple amino acids, cysteine can be determined without interference from large excesses of amino acids in protein hydrolysates.

A. O. Jones

3585. **Colorimetric micro-determination of thiols in alcoholic medium with N-ethylmaleimide.** J. Broekhuysen (Service de Recherches, C.E.R.I.A., Brussels, Belgium). *Anal. Chim. Acta*, 1958, **19** (6), 542–547 (in French).—Thiols react with N-ethylmaleimide (**I**) in alkaline abs. *iso*propyl alcohol (**II**) to give a red colour, and the necessary experimental conditions for the satisfactory quant. application of this reaction have been studied. Mix 0·2 ml of **I** soln. in **II** (0·5 *M*) with 1 ml of a soln. of the thiol in **II**. Set aside for 4 or 5 min., add 1 ml of KOH soln. in **II** (0·025 *N*), mix, and add 2·5 ml of **II**. Measure the extinction at 515 mμ, 10 min. after the addition of KOH. Beer's law is obeyed between 0·01 and 0·10 μg of –SH and the colour is stable for 15 min. T. R. Andrew

3586. **Determination of alkylarylsulphonates by ultra-violet absorption.** R. M. Kelley, E. W. Blank, W. E. Thompson and R. Fine (Colgate-Palmolive Co., Jersey City, N.J., U.S.A.). *Bull. A.S.T.M.*, 1959, (237), 70–73.—In the spectrophotometric procedure described, the strong max. extinction of a dil. aq. soln. (≃10 to 12 p.p.m.) of an alkylarylsulphonate is measured at 224 mμ in a 1-cm quartz cell *vs.* a water blank. Readings do not vary with pH and conform to Beer's law. A quartz flow-cell (light path ≃0·03 cm) inserted in series in the normal assembly enables higher concn. (0·3 to 0·5 g in 1 litre) to be used. Interferences (mainly compounds containing the phenyl chromophore) and their control are discussed; the extinction of phosphates, silicates, CO_3^{2-} and carboxymethylcellulose is low. The accuracy is equiv. to that of the alternative routine methods for most commercial detergents. W. J. Baker

3587. **Spot tests for aromatic compounds using 2:4:7-trinitrofluorenone.** H. T. Gordon and M. J. Huraux (Univ. of California, Berkeley, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 302–307.—Many aromatic compounds form coloured complexes when 10 μg is spotted on filter-paper and sprayed with 2:4:7-trinitrofluorenone in benzene (0·5%). Some compounds show brilliant u.v. fluorescence. Qualitative information of the structure of unknown compounds can be easily derived from the colour and fluorescence reactions and by determination of the solubility of the complex in *iso*octane and ethanol. The procedure is suitable for paper chromatography. Data for over 300 compounds are listed.

G. P. Cook

3588. **Rapid determination of aliphatic hydrocarbons in benzene of special reagent grade by gas chromatography.** Tsugio Takeuchi and Fukuzoo Hayakawa (Fac. of Engng, Yamanashi Univ., Motoyanagi-cho, Kofu). *Japan Analyst*, 1958, **7** (11), 712–716.—When pure benzene was submitted to gas chromatography (stationary phase, tritolyl phosphate, Carbowax or dioctyl phthalate; carrier gas, H; rate of flow, 60 ml per min.; sample, 0·1 ml), four peaks were observed before the peak of benzene appeared. Three of them were identified as *n*-heptane (≃0·15%), *cyclo*hexane (≃0·08%) and methyl*cyclo*hexane (≃0·07%), and their amounts were determined with diethyl ether as internal standard. The ratio of the peak height of the aliphatic hydrocarbons to that of ether is proportional to the ratio of their weights. K. Saito

3589. **Investigations on the relationship between gas-chromatographic ratios and vapour-pressure ratios. I. Aromatic hydrocarbons.** D. Jentzsch and G. Bergmann (Inst. f. Spektrochem. u. angew. Spektroskopie, Dortmund-Aplerbeck, Germany). *Z. anal. Chem.*, 1959, **165** (6), 401–415.—The gas-chromatographic retention ratios of aromatic hydrocarbons were measured at various temp. and were compared with the calculated vapour-pressure ratios; the Clausius - Clapeyron and Antoine formulae were utilised for the vapour-pressure calculations. Good agreement (to the first place of decimals) between the two ratios were obtained and the deviations occurring between these values are discussed with the aid of the Herrington equation. Diagrams of log retention ratio *vs.* log v.p., v.p. ratios and other functions are of value both for practical and theoretical applications. *o*-Xylene was used as the reference standard for the calculation of the retention and v.p. ratios.

G. P. Cook

3590. **Spot test for phenols by a modified indophenol method.** Takanobu Itai and Shozo Kamiya (Nat. Hygienic Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *Japan Analyst*, 1958, **7** (10), 616–618.—Autoxidation suffices for the formation of indophenols from *p*-aminophenol (**I**) (prep. described) and various phenols, including di- and tri-hydric phenols, *o*-, *m*- and *p*-amino- and *p*-chloro-phenols and naphthols, the colour produced being characteristic for each phenol. This test is as sensitive as that of Gibbs (*J. Biol. Chem.*, 1927, **72**, 649). Amines and sulphur compounds do not interfere. One drop of the sample soln. is mixed with one drop of NaOH soln. (2%) (and a few drops of ethanol when necessary) and **I** soln. (0·1 mg per ml, 0·5 ml). K. Saito

3591. **Gas chromatography of monohydric phenols.** J. Janák, R. Komers and J. Šíma (Lab. for Anal. of Gases, Acad. Sci., Brno, Czechoslovakia). *Chem. Listy*, 1958, **52** (12), 2296–2310.—The relation of the structure of the molecule in the solid phase to the selectivity of the separation of monohydric phenols is discussed. The specific elution vol. (chromatographic spectrum) of 19 phenols in polar and non-polar phases have been measured. In

practice, the use of Apiezon I or dimethylpolysiloxane has been found suitable for separation according to the C number, whereas the use of erythritol and the ethylene mercaptal of D-glucose is advantageous when separating according to the steric hindrance of the hydroxyl group. The temp. is kept between 150° and 170° during the separation. The reproducibility and accuracy of the areas under the chromatographic elution curve have been examined in relation to the weight and molar composition of the mixture, with H and N as carrier gases. J. ZÝKA

3592. **Spot tests for phenols and alkylated anilines based on the Duff formylation.** F. Feigl and E. Jungreis (Lab. Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Analyst*, 1958, **83**, 666–669.—The formylation of phenols and dialkylanilines as developed by Duff (*J. Chem. Soc.*, 1941, 547; 1945, 226) has been extended to monoalkylanilines. It is effected by mixing in a micro test-tube a drop of the sample soln. in ethanol or diethyl ether with a mixture of crystalline oxalic acid and hexamine (1:1), warming to remove the solvent, heating the tube in a glycerol bath at 160° for 1 to 2 min. and adding a drop of a reagent made by dissolving 10 g each of hydrazine sulphate and Na acetate in 100 ml of water. The suspension (a drop of water may be added) is dried on filter-paper. If the sample contains phenols, the stains exhibit a blue-green or orange fluorescence in u.v. light. With phenol and cresols the *o*-hydroxyaldehydes formed volatilise, and a filter-paper moistened with the reagent is held over the melt. The failure of certain phenolic bodies to respond to the test is discussed. The procedure for the detection of mono- and di-alkylanilines is similar to that for phenols, except that the cooled reaction mixture is treated with one or two drops of water, and the soln. or suspension is placed on filter-paper impregnated with a soln. of benzidine in ether. An orange stain indicates a positive result. A. O. JONES

3593. **Metol (*p*-methylaminophenol sulphate) photographic grade.** British Standards Institution (2 Park Street, London). B.S. 3105:1959, 12 pp.—Standards of quality are laid down, and apparatus and procedures specified for the determination of identity (melting-point of the nitroso derivative compared with that of an authentic specimen), volatile matter, ash, solubility in water, oxidisable matter, and iron and heavy metals by limit tests, and for the determination of *p*-aminophenol and the detection of *p*-di(methylamino)benzene. E. J. H. BIRCH

3594. **Hydroquinone (quinol, *p*-dihydroxybenzene) photographic grade.** British Standards Institution (2 Park Street, London). B.S. 3103:1959, 10 pp.—Standards of quality are laid down, and apparatus and procedures specified for the determination of melting-point, identity (mixed melting-point), ash, solubility in 5% acetic acid soln., oxidisable matter, and iron and heavy metals by limit tests. E. J. H. BIRCH

3595. **An analytical method for the determination of the cresols, based on their capillary-active properties.** E. Angelescu and Y. Davidescu. *Stud. Cercet. Chim., Bucharest*, 1958, **6** (2), 213–231.—The proposed method for the determination of *o*-, *m*- and *p*-cresol in aq. soln. is based on the variation of surface tension when these isomers are titrated with NaOH soln. The curve of concn. of NaOH soln. against surface tension consists of 3 parts. The first straight portion shows a linear increase of surface tension with increase of addition of NaOH, corresponding to the removal of cresol molecules. The last portion shows a constant max. value of surface tension when all the cresol has been converted into the Na salt. The intermediate curved portion is due to the gradual dilution of the system and hydrolysis. The apparent end-point is obtained by the intersection of the projected straight portions. Curves obtained with known concn. gave low results from stoicheiometric calculations when the concn. of *o*-cresol was >0·7% and *m*-cresol >0·35%. From these curves, empirical correction factors were obtained which, for concn. up to 2·3, 1·75 and 1·63% of *o*-, *m*- and *p*-cresol, respectively, gave errors ≯0·8%. H. SHER

3596. **Physico-chemical investigation of — -phenylacetylcarbinol [1-hydroxy-1-phenylpropanone] and methylbenzoylcarbinol [1-benzoylethanol]. II. Polarographic determination of — -phenylacetylcarbinol, methylbenzoylcarbinol and benzaldehyde in the presence of each other.** M. Fedoroňko (Dept. Pharm. Chem., and Biochem., Chem. Inst. Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1958, **12** (12), 690–698.—The quant. polarographic determination of 1-hydroxy-1-phenylpropanone (**I**), 1-benzoylethanol (**II**) and benzaldehyde (**III**) has been studied. Different $E_{\frac{1}{2}}$ values in the medium of 0·5 *M* aq. NH_3 with 0·5 *M* NH_4Cl permitted the determination of **II** or **III** in the presence of **I**. By using a soln. in a mixture of 0·025 *M* methylamine and 0·11 *M* methylamine hydrochloride (pH 10), the determination of **III** (after conversion to a Schiff's base) in the presence of **II** (which does not react with methylamine) can be carried out. *Procedure*—Add a 1% ethanolic soln. of the sample (0·5 ml) to the buffer soln. (0·5 *M* aq. NH_3 - 0·5 *M* NH_4Cl) (3·5 ml), remove O with a stream of N and immediately register the polarographic wave. Compare with a calibration curve. J. ZÝKA

3597. **Colorimetric determination of (−)-phenylacetylcarbinol.** O. Bauerová and Š. Bauer (Dept. Pharm. Chem. and Biochem., Chem. Inst. Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1959, **13** (1), 38–41.—(−)-Phenylacetylcarbinol (**I**) reacts with blue tetrazolium (**II**) yielding a colour suitable for analytical purposes. The method is not influenced by the presence of benzaldehyde and can be used in controlling technological products of **I** with an accuracy of ±3%. *Procedure*—Into a 50-ml flask place an ethanolic soln. of the sample (10^{-5} to 10^{-6} g of **I**), add 1 ml of freshly prepared **II** soln. (0·2% ethanolic), 1 ml of 0·05 *N* NaOH in 25% *iso*propyl alcohol and set aside for 10 to 15 min., with occasional shaking. Dilute to vol. with a soln. of 0·01 *N* acetic acid in 90% *iso*propyl alcohol and measure the extinction with the use of a blue-green filter (490 mμ). J. ZÝKA

3598. **Detection of arylidene arylhydrazones anp thereby differentiation of aromatic aldehydes and ketones.** E. Sawicki, T. W. Stanley and T. R. Hauser (R. A. Taft San. Engng Center, U.S. Dept. of Health, Education and Welfare, Cincinnati, Ohio, U.S.A.). *Chemist Analyst*, 1958, **47** (4), 87–88.—To a few ml of a soln. of a hydrazone in 2-methoxyethanol (**I**) add 0·1 ml of a fresh 0·5% soln. of *p*-nitrophenyldiazonium fluoroborate in **I**, followed by 0·2 ml of 10% aq. tetraethylammonium hydroxide soln. Dilute the mixture to 10 ml with **I**, note the colour, and determine the absorption

spectrum from 400 to 700 mμ against the appropriate blank. Colours, wavelengths of maximum absorption, and sensitivities are listed for 10 compounds. All arylidene arylhydrazones tested, except those containing pyridine rings or nitro or amino groups, gave purple, blue or green colours, while hydrazones from all arylalkyl, dialkyl and diaryl ketones gave a (negative) yellow colour. If the reaction is carried out in a micro test-tube with one-twentieth of these quantities of reagents, sensitivities of the order of 0·1 μg can be obtained, and the same order of sensitivity is attained in a filter-paper spot-test procedure. R. E. ESSERY

3599. **Potentiometric titrations of weak acids in non-aqueous solvents. I. Benzoic acid, ε-cyclohexylcaproic acid, *p*-cresol and 1-naphthol.** D. H. Mathews and T. R. Welch (British Petroleum Co., Ltd., Sunbury-on-Thames, Middx, England). *J. Appl. Chem.*, 1958, **8** (11), 701–710.—Potassium methoxide (0·1 *N*), standardised with benzoic acid, is used for the titration of organic acids such as occur in bitumens and tars. Benzene - methanol (3:1), benzene - *iso*propyl alcohol (3:1), or acetone is suitable for carboxylic acids, the first being especially so; the presence of phenols makes the end-point less sharp. For acid - phenol mixtures, ethylenediamine - benzene (3:1) or *n*-butylamine is used; CO_2 in solvents is neutralised with K methoxide before titration. The electrode system platinum - tungsten was selected, isolation of the reference electrode being necessary to avoid reversal of the slope of the titration curve near the neutralisation point. The e.m.f. (E) *vs.* vol. of titrant (V), and subsequently V *vs.* dE/dV are plotted to give the end-point. The antimony - platinum electrode system is suitable for titrations in ethylenediamine - benzene. Reproducibility is ±1·25% of V for the first three solvents, but rather poorer for the two basic solvents. Indicator titrations of similar mixtures are somewhat more precise.

II. Hydroxybenzoic acids and dihydric phenols in *n*-butylamine. D. H. Mathews and T. R. Welch. *Ibid.*, 1958, **8** (11), 710–715.—The carboxyl and hydroxyl groups of hydroxybenzoic acids can be titrated accurately with K methoxide in *n*-butylamine if the antimony - glass electrode system is used. The hydroxyl groups of dihydric phenols can also be determined, except for the second hydroxyl group in 4-methylcatechol. The platinum - tungsten electrode system is suitable for the determination of the carboxyl group only. Acids titrated include salicylic acid, *p*-hydroxybenzoic acid, 2:4- and 2:5-dihydroxybenzoic acid; dihydric phenols used were resorcinol, quinol, 3-methylcatechol, 4-methylcatechol, and 1:5- and 1:6-dihydroxynaphthalene. The effect of the substitution position is discussed; groups in *ortho* positions increase the dissociation of the carboxyl group, and lessen that of the hydroxyl group, while the reverse is true for *para* substitutions. For the *meta* position no marked effects are observed.

P. D. PARR-RICHARD

3600. **Oxidative metabolism of phenylacetic acid by *Penicillium chrysogenum* A176. XIV. Biological determination of *p*-hydroxybenzoic acid.** Masao Isono (Inst. for Fermentation, Juso-nishinocho, Higashiyodogawa-ku, Osaka). *J. Agric. Chem. Soc. Japan*, 1958, **32** (6), 433–435.—*p*-Hydroxybenzoic acid (**I**) is determined biologically with a strain of *Pseudomonas*, by the use of a Warburg manometer. The method is similar to that for phenylacetic acid (*Ibid.*, 1953, **27**, 193). A linear relationship holds between the concn. of **I** and the vol. of evolved O. Protocatechuic acid interferes, but benzoic, salicylic, *m*-hydroxybenzoic and gentisic acids, phenol and catechol do not.

K. SAITO

3601. **Reactivity of catecholamines, 5-hydroxyindoles and phenols with blue tetrazolium.** H. Rosenkrantz (Worcester Foundn. for Exp. Biology, Shrewsbury, Mass., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **81** (1), 194–203.—A comparative study is made of the reaction rates and intensities of 27 compounds with blue tetrazolium (**I**) and with the $FeCl_3$ - 2:2′-dipyridyl reagent (**II**) of Emmerie and Engel. The reactivity of catecholamines with **I** was about four times that of 5-hydroxyindoles or α-ketolic steroids, and an adaptation of the test to the assay of urinary catecholamines is described. Although less sensitive, the reaction with **II** was of value in distinguishing catecholamines from the corresponding N-methylated derivatives. W. H. C. SHAW

3602. **Spectrophotometric determination of stabilised diazonium compounds.** H. M. Rosenberger and C. J. Shoemaker (A. B. Dick Co., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 204–206.—The absorption spectra of the diazonium compounds investigated show strong absorption bands in the 350 to 400-mμ region, which are attributed to the –N:N– chromophore group. The max. at 380 mμ obeys Beer's law in the concn. range 1 to 10 p.p.m. The sample is measured in aq. soln. The results agreed within 1% with those obtained by the nitrometer procedure, and the method was successfully applied to wax mixtures (used as paper-coating materials). G. P. COOK

3603. **Paper chromatography of aromatic nitro compounds.** M. Perpar, M. Tišler and Ž. Vrbaški (Inst. f. organ. Chem., Univ., Ljubljana, Yugoslavia). *Mikrochim. Acta*, 1959, (1), 64–67.—Filter-paper (S. & S. 2043b) is impregnated with a petroleum fraction (boiling-range 160° to 190°) and allowed to dry for 30 min. in air; 0·05 ml of a 0·1% ethanolic soln. of the sample is spotted on the paper and developed for 12 to 15 hr. at 24° with either 96% ethanol - water (4:3) or 96% ethanol - water (3:5). R_F values are quoted for 18 aromatic nitro compounds. In some cases the compounds were eluted completely and the eluate examined spectrophotometrically; for amounts of 2 to 6 μg, recoveries with a precision of ±5% are quoted. In other cases the errors were too high for the method to be of practical use.

T. R. ANDREW

3604. **Infra-red analysis of the isomers of NN-diethyltoluamide.** W. H. Clark (Hercules Powder Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 197–199.—Two procedures are described: one for mixtures containing a high *m*-isomer content (60 to 90%), a low *p*-isomer content (10 to 40%) and no *o*-isomer, and the other procedure is applicable to *o*-isomer concn. of 5 to 10%. The *m*- and *p*-compounds are determined by conventional i.r. techniques but a compensation procedure is used for the *o*-compound to reduce interference by the *m*-isomer. The precision for the first method (95% confidence limits) is ±0·8% absolute for duplicate determinations of a mixture containing 85 and 15% of the *m*- and *p*-isomers, respectively; recoveries are >99 and >98%,

respectively. The precision for the determination of the *o*-isomer is ±0·2% absolute at a concn. of 5%; recoveries are >92%. G. P. Cook

3605. **Fluorescence of some salicyloyl hydrazones.** P. S. Chen, jun. (Nat. Heart Inst., Nat. Inst. of Health, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 296–298.—*o*-Hydroxybenzaldehyde, *p*-hydroxybenzaldehyde and *p*-dimethylaminobenzaldehyde form salicyloyl hydrazones with fluorescence characteristics that are relatively specific compared with those of other salicyloyl hydrazones, which either do not fluoresce or do so with excitation and fluorescence maxima similar to those of salicyloyl hydrazine. The maximal excitation of the three compounds occurs at 390 mμ and the fluorescence at 470 mμ, as compared with 350 and 425 mμ for salicyloyl hydrazine.

G. P. Cook

3606. **Determination of small amounts of 2-naphthylamine in 1-naphthylamine.** G. Parravano (ACNA, Cegnio, Italy). *Chim. e Ind.*, 1959, **41** (1), 30–33.—The method described is based on the colorimetric reaction of furfuraldehyde with primary aromatic amines. The conditions under which the reaction rate is lowest for the 1- and highest for the 2-isomer are established [in ethanol (25 ml) with dil. acetic acid (0·5 ml) at 20° for ⩾90 min.] and a quant. determination is developed which is based on extinction measurements at 550 mμ. A suitable calibration curve is given. Data are plotted for 1-naphthylamine containing 0·5, 5·0 and 10% of the 2-isomer. The method can also be applied to nitronaphthalenes, after reduction to the amines. C. A. Finch

3607. **Physical properties of anthraquinone and its derivatives. I. Infra-red spectra.** H. Bloom, L. H. Briggs and B. Cleverley (Dept. of Chem., Univ. of Auckland, New Zealand). *J. Chem. Soc.*, 1959, 178–185.—The infra-red spectra of 60 anthraquinone derivs. are listed, and the reason for differences in absorption is discussed. A summary of diagnostic features is given, showing that the spectrum of an individual compound is unique. E. J. H. Birch

3608. **Colorimetric determination of (+)-pulegone with 3:5-dinitrobenzoic acid.** D. H. E. Tattje (Rijksuniv., Gronigen, Netherlands). *Pharm. Weekbl.*, 1958, **93** (24), 1048–1053.—*Procedure*—To 4 ml of a soln. containing 0 to 2·7 mg of (+)-pulegone in ethanol add a 4% soln. of 3:5-dinitrobenzoic acid in ethanol (5 ml) and 3 *N* aq. NaOH (2 ml). Set aside for 40 min. and measure the extinction at 5375 A against a reagent blank. The calibration curve conforms to Beer's law up to 2·7 mg of (+)-pulegone. The temp. must be maintained at 20° for all determinations. With two out of three samples of pennyroyal oil, both of higher density than (+)-pulegone and darker than the third sample, the colorimetric method gave lower results than the neutral sulphite method. With the third sample and with pure (+)-pulegone, the results of the two methods were in good agreement. Piperitone and piperitenone, which may also occur in pennyroyal oil, give the same reaction. Menthone does not react with 3:5-dinitrobenzoic acid. G. Burger

3609. **Pyridine.** British Standards Institution (2 Park Street, London). B.S. 3096–97:1959, 16 pp.—Standards are laid down for pyridine (99% minimum purity; B.S. 3096) and pyridine (90% minimum purity; B.S. 3097). Apparatus and procedures are specified for the determination of colour, distillation range, residue on evaporation, miscibility with water, and clearing-point.

E. J. H. Birch

3610. **Pyridine bases.** British Standards Institution (2 Park Street, London). B.S. 3098–99:1959, 20 pp.—Specifications are laid down for pyridine bases, 90/160 (B.S. 3098) and 95/180 (B.S. 3099). Apparatus and procedures are specified for the determination of colour, distillation range, water, total bases, non-basic material other than water, and primary bases, and for tests for miscibility with water and 95% (v/v) ethanol, and for pptn. with cadmium chloride and for the colour of the ppt. with Nessler reagent. E. J. H. Birch

3611. **Determination of pyridine-2-aldoxime methiodide and its corresponding stereoisomer by ultraviolet analysis.** E. I. Ellin and A. A. Kondritzer (Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 200–201.—A method for the determination of pyridine-2-aldoxime methiodide (**I**) in the presence of its acid hydrolytic products is based on the fact that the *anti*-isomer exhibits absorption maxima at 292 mμ in acid soln. and at 333 mμ in alkaline soln. Neither the *syn*-isomer nor the acid hydrolytic products of **I** interfere at these wavelengths. The accuracy is ≃100% in the concn. range of 0 to 10 μg per ml. Because **I** yields hydroxylamine on acid hydrolysis, the formation of pyridine-2-carboxaldehyde methiodide (**II**) was indicated and the spectrum of this compound was also investigated. Determinations of **II** gave recoveries ≃100% in the 1 to 10-μg range.

G. P. Cook

3612. **Phosphorescence spectra and analysis of some indole derivatives.** S. Freed and W. Salmre (Chem. Dept., Brookhaven Nat. Lab., Upton, N.Y., U.S.A.). *Science*, 1958, **128**, 1341–1342.—A rotating phosphoroscope between two monochromators disposed at right angles is employed to measure the spectra of soln. frozen at low temp. (77° K). The method is superior to spectrofluorimetry, some indole derivatives indistinguishable by their fluorescence being easily differentiated by phosphorescence measurements. H. F. W. Kirkpatrick

3613. **Studies on furfuraldehyde. VI. The colorimetric determination of furfuraldehyde with aniline in the presence of some mineral acids.** D. A. Isăcescu, S. Biller and M. Macavei-Beştelei. *Stud. Cercet. Chim., Bucharest*, 1958, **6** (2), 247–253.—In previous work (*cf.* Isăcescu and Biller, *Stud. Cercet. Biochim.*, 1958, **1**, 2) it was observed that ethanolic soln. of aniline and furfuraldehyde (**I**) gave a rose-red colour which followed the Beer - Lambert law. The conditions for determinations of **I** with a Duboscq type of colorimeter have been investigated. *Procedure*—An ethanolic soln. of aniline (1 *M*) (4 ml) and **I** soln. (4 ml) is treated with 0·02 ml of HCl, H_2SO_4 or H_3PO_4 (0·01 *N*). The rose-red soln. is warmed for 1 min. on the water bath, then cooled, and left at room temp. for 30 min. The colour is then compared with a standard. Standard soln. recommended are 4 ml of **I** soln. (0·1%) for concn. of 0·2 to 0·5% in a 20-mm tube (1% for concn. of 2 to 3% in a 10-mm tube). For 1 ml of a standard of 0·1% good results are obtained with concn. between 0·05 and 0·5% at a depth of 5 mm. A preliminary trial with a standard soln. is necessary

to establish whether the unknown soln. must be diluted so that the subsequent colour developed falls within the range of the standard.

H. SHER

3614. **Determination of closed flash-point of petroleum products by means of the Pensky-Martens apparatus.** British Standards Institution (2 Park Street, London). B.S. 2839:1957 (Amendment No. 1, pub. 10.4.59), 2 pp.—The amendments include reference to I.P.34/58 and changes in the dimensional limits of the apparatus, in the precision and in the specification of the thermometers. Clause 3, the preparation of the sample, is omitted.

G. BURGER

3615. **Separation of paraffin - cycloparaffin portion of naphtha into normal, branched and cycloparaffins.** M. S. Norris and J. G. O'Connor (Gulf Res. and Development Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 275–279.—The saturate fraction of a naphtha was charged on a column of 5-A molecular sieves. The branched and cyclic components were eluted with *iso*pentane and the straight-chain compounds removed with *n*-pentane. The branched and cyclic material was separated by chromatography using a high pore-volume silica gel saturated with 2-(2-methoxyethoxy)ethanol. The column was eluted with a perfluorocyclic ether ($C_8F_{16}O$), the branched material being eluted first in high purity and the cyclic compounds last, intermediate fractions showing decreasing contents of branched and increasing contents of cyclic compounds.

G. P. COOK

3616. **Mass-spectrometric analyses of medium-viscosity lubricating oils.** M. L. André and M. J. O'Neal, jun. (Res. Lab., Shell Oil Co., Houston, Tex., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 164–169.—Seven representative medium-viscosity oils have been examined by mass spectrometry and the relation of the *iso*alkane and condensed and non-condensed *cyclo*alkane content to the viscosity index determined. An examination has been made of the relation of the depth of extraction of the oil with furfuraldehyde to the aromatic content of the raffinate.

K. A. PROCTOR

3617. **Insulating oil for transformers and switchgear.** British Standards Institution (2 Park Street, London). B.S. 148:1959, 40 pp.—This Standard replaces B.S. 148:1951. The evaporative loss test is deleted. The procedure for acidity determination has been improved by substituting ethanolic KOH for aq. KOH. An appendix on thermometer specifications is included. The standard applies to unused insulating oils, and not to high-viscosity oils, cable and capacitor oils or impregnating oils.

G. BURGER

3618. **Spectrophotometric analysis of distillable low-temperature tar bases.** C. Karr, jun., and Ta-Chuang Lo Chang (Low-temp. Tar Lab., Bur. of Mines, Morgantown, W. Va., U.S.A.). *J. Inst. Fuel*, 1958, **31**, 522–527.—Bases amounting to 0·31% (w/w) of a low-temp. (480° to 510°) tar from a high-volatile bituminous coal were separated by vacuum fractionation (125° and 0·133 mm) and acid extraction (*cf.* Fisher and Eisner, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 213) and divided into 35 fractions by distillation at 25° to 186° at 80 mm to 3 mm. Comparison of the u.v. and i.r. absorption spectra of the fractions with those of pure compounds showed the presence of 17 pyridine derivatives (*P*) amounting to 35% (w/w) of the bases, 23 quinolines (*Q*) (46%), and 11 anilines (*A*) (16%). Besides alkyl (mainly methyl) homologues, *P* included *cyclo*penteno- and phenyl-pyridines; *Q* included benzoquinolines, and *A* included N-benzylanilines and 2-naphthylamine.

A. R. PEARSON

3619. **Methods for the analysis and testing of coal and coke. Part 7. Ultimate analysis of coke.** British Standards Institution (2 Park Street, London). B.S. 1016: Part 7:1959, 36 pp.—In this Standard, which deals with the determination of C, H, N and S, the Liebig method for the determination of C and H has been modified and an alternative method introduced. A semi-micro method has been substituted for the macro-Kjeldahl method for N, and the Eschka method for total S has been modified. The section on preparation of the sample has been transferred to the revised B.S. 1017.

G. BURGER

3620. **Methods for the analysis and testing of coal and coke. Part 11. Forms of sulphur in coal.** British Standards Institution (2 Park Street, London). B.S. 1016:Part 11:1959, 13 pp.—This Standard deals with the determination of sulphate, and pyritic and organic S. The method of Powell and Parr (*U.S. Bur. Mines Tech. Paper No.* 254) has been modified. Pyritic S is obtained from the determination of total iron and non-pyritic iron. Organic S is determined by difference. The section on the preparation of the sample has been transferred to B.S. 1017.

G. BURGER

3621. **Sampling and testing gelatins.** British Standards Institution (2 Park Street, London). B.S. 757:1959, 47 pp.—The methods for initial and final sampling of sheet, cake, leaf, pearl, powdered, granulated, flake and kibbled gelatin, and for the preparation of the laboratory sample, are laid down. Procedures and apparatus are specified for the determination of moisture, jelly strength (finger test and Bloom-type gelometer), viscosity, melting-point, water absorption, solubility of partially swollen sheet, keeping quality, pH, grease, ash, SO_2, chlorides, arsenic, heavy metals, lead, copper and zinc.

E. J. H. BIRCH

3622. **Sampling and testing glues.** British Standards Institution (2 Park Street, London). B.S. 647:1959, 37 pp.—Methods are given for the initial and final selection of the sample, and the preparation of the laboratory sample, for sheet, cake, powdered, pearl, cube, granulated, flake, and kibbled glues, and slab, jelly and liquid glues. Methods and apparatus are specified for the determination of moisture, jelly strength (finger test and Bloom-type gelometer), viscosity, melting-point, water absorption, foam, keeping quality, pH, grease, ash, SO_2, chlorides, and joint strength in shear.

E. J. H. BIRCH

3623. **Physicochemical characterisation of essential-oil constituents and their derivatives by modern instrumental techniques.** L. Levi, J. L. Thomson, J. C. Evans, H. Bernstein, S. A. Forman and N. M. Miles (Food and Drug Lab., Dept. of Nat. Health and Welfare, Ottawa, Canada). *Perfum. Essent. Oil Rec.*, 1958, **49** (11), 715–728.—The application of physicochemical methods to the analysis of essential oils is discussed, with a survey of relevant literature. Figures for the conventional physicochemical constants are tabulated, and i.r. and Raman spectra data are given for eugenol, its methyl and acetyl

ethers, *iso*eugenol, its methyl, acetyl and benzyl ethers, and anethole. X-ray powder diffraction data are recorded for *iso*borneol, (−)-borneol, *iso*bornyl, (±)-bornyl and (−)-bornyl *p*-nitrobenzoates, the 2:4-dinitrophenylhydrazones of (±)-camphor and (−)-camphor, (±)-camphor semi carbazone, and (±)- and (−)-pinonic acids, by using film and diffractometer methods, with cobalt radiation and iron filter. The results for the various compounds, and the advantages and limitations of the different techniques for their characterisation and identification, are discussed.
R. E. ESSERY

3624. **Identification of colouring matters by paper chromatography. Various applications.** Z. Molester. *Ann. Chim., Paris*, 1958, **3** (11–12), 771–814.—After a preliminary literature survey, apparatus is described for the paper chromatography of synthetic organic dyes by the ascending technique at room temp. Eighty-five dyes, in 13 different chemical groups, were examined, with several solvent systems, and for each dye the following data are given—concn. of dye (0·1 to 0·25% aq. or alcoholic), most suitable solvent system, duration of chromatography (1·5 to 7 hr.), R_F value, colour of the spot in daylight and u.v. light before and after chromatography, and colour of the spot in daylight after treatment with 10% NaOH soln. and 10% HCl. The applications described, with manipulative details, include the comparison and identification of the colouring matters of lipsticks and lipstick stains, and the investigation of the colouring matters of liquid inks and those used in ball-point pens and of specimens of writing produced therewith. R. E. ESSERY

3625. **Bromination as a method for the analysis of triphenylmethane dyes.** M. Matrka (Res. Inst. Org. Synth., Pardubice-Rybitví). *Chem. Průmysl*, 1958, **8** (11), 583–585.—A 0·2 *N* bromate - bromide soln. (5·568 g of $KBrO_3$ plus 24 g of KBr in 1 litre) is used for the direct potentiometric determination of triphenylmethane dyes. *Procedure*—Dissolve the sample (0·1 g) in *N* HCl (100 ml) and titrate potentiometrically, with stirring, with 0·2 *N* $KBrO_3$ - KBr. Near the end-point the dye is pptd. The method is suitable for the determination of pure triphenylmethane dyes. The presence of compounds that readily react with bromine (*e.g.*, leuco-bases, intermediates such as Michler's ketone, Michler's hydrol and 4:4′-tetramethyldiaminodiphenylmethane) causes results higher than those obtained by another reductimetric determination with VSO_4, and the use of the procedure described is therefore limited. It is, however, useful for determining the leuco-bases of various dyes, *e.g.* malachite green. The mechanism of the bromination is discussed. J. ZÝKA

3626. **Determination of cellulose, and indirectly of household coal, in compost from town refuse.** L. J. Mebius (Inst. voor Bodemvruchtbarheid, Gronigen, Netherlands). *Chem. Weekbl.*, 1958, **54** (50), 711–715.—Samples are prepared by boiling the dried and ground compost (300 mg) with 80 ml of Scharrer - Kurschner reagent [70% aq. acetic acid containing 27·5 g of trichloroacetic acid and 68 ml of HNO_3 (sp. gr. 1·4) in 1 litre]. The residue is washed with reagent, water and acetone, dried and weighed. Cellulose is determined by heating one sample for 90 min. in a boiling-water bath with 15% (w/w) aq. H_2SO_4 (40 ml) and 2 *N* $K_2Cr_2O_7$ (25 ml), mixing 25 ml of the soln. with 0·22 *N* $FeSO_4$ (25 ml) and titrating the excess with 0·1 *N* $KMnO_4$. The coal content is then determined from the loss on ignition of a second prepared sample.
G. BURGER

3627. **Determination of nitrogen in nitrocellulose.** J. D. Mullen (African Explosives and Chem. Industries Ltd., Transvaal, S. Africa). *Anal. Chim. Acta*, 1959, **20** (1), 16–19.—An examination of the transnitration method of Stalcup and Williams (*cf. Anal. Abstr.*, 1955, **2**, 2468) indicated that the precision could be improved by altering the conditions of reduction. With the modified procedure, a series of ten determinations on a sample of KNO_3 containing 13·8% of N gave a standard deviation of ±0·014. W. T. CARTER

3628. **Rapid determination, without a nitrometer, of nitrogen for control of manufacture of nitrocellulose.** O. Frehden and Z. Nicolescu. *Rev. Chim., Bucharest*, 1958, **9** (12), 688–689.—The method consists in saponification of the nitrocellulose, reduction of the HNO_3 to NH_3, and its subsequent titration after distillation, these operations taking place in a special apparatus (illustrated). *Procedure for micro- or semi-micro determinations*—Nitrocellulose (5 to 10 mg, or 50 to 100 mg) is transferred to the reaction vessel by means of a small amount of a mixture of diethyl ether and ethanol or acetone; 5 to 15 ml of NaOH soln. (30%) and 0·5 to 2 ml of H_2O_2 (30%) are added, the funnel tap is closed and steam is passed in to the jacket of the reaction vessel. When the nitrocellulose is dissolved, 0·5 to 1 g of Devarda's alloy is washed in through the funnel with a little water, followed by more NaOH soln. The liberated NH_3 is distilled into 2% H_3BO_3 and titrated with 0·02 *N* H_2SO_4, with methyl red (0·1% in ethanol) or a mixture of 3 parts of bromocresol blue soln. (0·1%) and 1 part of methyl red soln. (0·1%), both in ethanol, as indicator. The results are consistently 0·10 to 0·13% higher than those from nitrometer determinations. H. SHER

3629. **Quantitative analysis of binary fibre mixtures containing Tricel (cellulose triacetate).** W. Armfield (Courtaulds Ltd., Droylsden, Manchester). *J. Text. Inst. Proc.*, 1959, **50** (1), P51–P55.—The fibre groups investigated are—wool, cotton, polyamide (nylon 66), polyester (Terylene), regenerated protein (Fibrolane BX), acrylic (Courtelle and Orlon 42), viscose rayon (Fibro), and secondary cellulose acetate (Dicel). In fibre mixtures of Tricel with Dicel, the latter is dissolved by extraction with 70% v/v aq. acetone; Tricel is removed from all the other mixtures by extraction with dichloromethane. O. M. WHITTON

3630. **Colorimetric determination of sulphur in rayon staple, cellulose acetate and poly(vinyl alcohol).** Hiroshi Terada and Masao Yosida (Otake Plant, Mitsubishi Rayon Co., Otake, Hiroshima-ken). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1958, **61** (10), 1301–1303.—The phosphoric acid - stannous chloride method (*cf.* Kiba *et al.*, *Anal. Abstr.*, 1958, **5**, 1874) followed by colorimetric determination of resulting H_2S with 4-aminodimethylaniline (**I**) was applied to the analysis of S in rayon staple, cellulose acetate and poly(vinyl alcohol). Conversion of S into SO_4^{2-} is effected by heating with HNO_3 and MgO. The standard deviation is ±0·0003% for ≃0·02% of S and the time taken for an estimation is ≃1 hr. *Procedure*—Wash the sample (1 g) with hot water (to remove oily substances), dry and mix a

0·1-g portion with MgO (50 mg) and HNO_3 (2 ml) in a glass vessel and heat first on a sand bath and then in an oven (700° to 800°) for 10 min. until nitrate is completely decomposed. Add conc. phosphoric acid (5 ml) containing Cr^{3+} and Sn^{2+}. [Heat H_3PO_4 under reduced pressure to 300°. Add $K_2Cr_2O_7$ (2 g) to the phosphoric acid (300 g), heat until the liquid becomes green, cool and add $SnCl_2$ (50 g) with heating to 300°.] Heat to 300° in a current of CO_2 (60 to 120 bubbles per min.) for 15 min. and pass the H_2S into Zn acetate (4%, 35 ml). Cool for 5 min. in a current of CO_2. Add **I** hydrochloride (0·5% in 500 ml of 18 *N* H_2SO_4 containing 5 ml of 6 *N* HCl) (1 ml) and $FeCl_3$ (10%, 1 ml) to the Zn soln., keep at 5° to 25° for 15 min., dilute to 5 ml and measure the extinction at 655 mμ.

K. SAITO

3631. **Quantitative chemical analysis of mixtures of viscose rayon and cotton.** British Standards Institution (2 Park Street, London). B.S. 3068: 1959, 7 pp.—The apparatus and procedure are described for the extraction of viscose rayon from mixtures with unscoured, scoured, kiered or bleached cotton with sodium zincate soln. The residue, corrected for loss in the solvent, is expressed as a percentage by weight of the sample, the viscose rayon being obtained by difference. The calculation of the results on the basis of dry weight or correct invoice weight is described. The accuracy of the results is discussed in relation to the proportion and nature of the cotton in the mixture.

A. M. SPRATT

3632. **Quantitative chemical analysis of binary mixtures of nylon 6 or nylon 66 and certain other fibres.** British Standards Institution (2 Park St., London). B.S. 3069:1959, 6 pp.—The apparatus and procedure are specified for the extraction of nylon from mixtures with cotton, viscose rayon, polyester fibre and wool (<25% of wool) with 80% formic acid. The residue, after correction for loss in the solvent, is expressed as a percentage by wt. of the mixture, and nylon is obtained by difference. The calculation of the results on the dry weight and correct invoice weight is described.

A. M. SPRATT

3633. **Method for the determination of conductivity, pH, water-soluble matter, chloride and sulphate in aqueous extracts of textile materials. Tentative textile standard No. 52.** Textile Institute. *J. Text. Inst., Proc.*, 1958, **49** (12), P724–P731.—Apparatus and procedures are specified.

3634. **Spectrophotometric determination of styrene in a styrene - methyl methacrylate copolymer.** A. V. Tobolsky, A. Eisenberg and K. F. O'Driscoll (Princeton Univ., N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 203–204.—Styrene is determined by measuring the absorbance of 1 mg of the copolymer in $CHCl_3$ soln. at 269 mμ. The absorbance is linear only up to ≃40% of styrene. G. P. COOK

3635. **Condensation of silicone resins (determination of silanol groups).** W. Noll, K. Damm and W. Krauss (Farbenfabr. Bayer Akt., Leverkusen, W. Germany). *Farbe u. Lack*, 1959, **65**, 17–24.—The resin, dissolved in chlorobenzene or dioxan, is heated under reflux for 2 hr. with *iso*cyanatobenzene, the excess of which is then caused to react with *iso*butylamine, and the residual amine is titrated with HCl. This method will determine OH present as H_2O as well as OH in silanol groups. To distinguish between the two types, a Karl Fischer determination is carried out; H_2O reacts immediately but silanol groups only slowly.

L. A. O'NEILL

3636. **Applications of infra-red spectroscopy in paint analysis and paint chemistry.** A. Reuter (Battelle Inst., Frankfurt/Main, Germany). *Farbe u. Lack*, 1959, **65**, 25–36.—Examples of the uses of infra-red spectroscopy in the following problems are given, with illustrative spectra—analysis of solvent mixtures; identification of vinyl polymers and polyesters; examination of insoluble films (*e.g.*, of polybutadiene, phenolic and urea resins, after initial pyrolysis); the mechanism of curing of polyurethanes; changes following high-energy irradiation of polyethylene. L. A. O'NEILL

3637. **Methods of testing raw rubber and unvulcanised compounded rubber. Part 2. Methods of chemical analysis.** British Standards Institution (2 Park Street, London). B.S. 1673, Part 2:1954 (Amendment No. 3, pub. 10.2.59), 10 pp.—The amendment specifies procedures for the determination of Mn in natural raw rubber, and of Cu (<10 p.p.m.) in raw and unvulcanised compounded rubber using a wet-oxidation method and in natural raw rubber by dry-ashing (two methods).

B. B. BAUMINGER

3638. **Methods of testing vulcanised rubber. Part B17. Determination of total copper.** British Standards Institution (2 Park Street, London). B.S. 903: Part B17: 1959, 7 pp.—The determination of trace amounts of Cu is based on a wet oxidation of 2 g of sample with conc. H_2SO_4 and HNO_3. Iron is complexed with ammonium citrate and, after making ammoniacal, the soln. is shaken with a measured amount of a $CHCl_3$ soln. of Zn diethyldithiocarbamate. The yellow $CHCl_3$ layer is transferred to a stoppered flask containing anhyd. Na_2SO_4 and its extinction is measured at 435 mμ. A reagent blank is carried out side by side with the test. The preparation of a calibration graph is described. B. B. BAUMINGER

3639. **Methods of testing vulcanised rubber. Part B19. Preparation and examination of water extract.** British Standards Institution (2 Park Street, London). B.S. 903: Part B19: 1958, 8 pp.—The method consists in boiling the rubber sample with water for 1 hr.; the water extract is used for the determination of total water-soluble matter, free acid or alkali, chloride, sulphate, pH value, electrical resistivity of the extract and a test for the presence of ammonium salts. The procedures specify a test portion of 5 to 15 g of the prepared sample and require an amount of water 20 times the weight of the test portion. The total minimum vol. of water required for all tests is 95 ml.

B. B. BAUMINGER

3640. **Methods of testing vulcanised rubber. Parts G1 to G9. Methods of testing rubber proofed fabric.** British Standards Institution (2 Park Street, London). B.S. 903: Parts G1 to G9: 1957, 34 pp.—General purpose tests which are regarded as common to all types of proofing are described, *i.e.*, selection of samples and test pieces; weight of proofing; state of vulcanisation (heat-cured and cold-cured vulcanisates); adhesion of proofing layers (ply and face adhesions); waterproofing (low- and high-pressure methods); breaking strength in tension; water extract; accelerated ageing (oven and oxygen pressure methods); and bend modulus stiffness. B. B. BAUMINGER

3641. **Colorimetric method for determination of protein in casein.** A. Marchenko (Tech. School, Chashinsk). *Molochnaya Prom.*, 1957, **18** (12), 28–29.—The use of the biuret test for the determination of protein in technical casein is described. Place ≃0·5 g of casein in a 50-ml beaker with 5% NaOH soln. (30 ml) and stir every 3 to 4 min. After 20 to 25 min., place the beaker in water at 45° to 50° and stir the mixture every 2 to 3 min. until either a colloidal soln. or a uniform mass of fine casein flakes is formed (usually 5 to 10 min., and 20 to 25 min. is required to dissolve acid and rennet casein, respectively). Transfer the mixture to a 50-ml flask and dilute to vol. Mix thoroughly and quickly pipette 2 ml of the soln. into a test-tube. Add water (8 ml), mix, add 5% $CuSO_4$ soln. (1 ml), mix again and then add 30% NaOH soln. (1 ml). Mix thoroughly for 1 min. and allow to stand for 1·5 hr. Read the clear violet-blue supernatant liquid in a colorimeter with casein standards closest in colour to the unknown. The method gives results in good agreement with those for the Kjeldahl method. CHEM. ABSTR.

3642. **Infra-red quantitative analysis data.** *Anal. Chem.*, 1959, **31** (2), 316.—The following data are given. **Determination of 2-nitronaphthalene in 1-nitronaphthalene,** R. E. Seeber, J. L. Alexander and H. J. McCarthy. **Determination of 2-naphthol in 1-naphthol,** R. E. Seeber and R. G. White.

See also Abstracts—**3370**, Analytical use of diarylborinic acids. **3393**, Determination of H_2O in organic solvents. **3425**, Determination of Al and Ti in polyethylene. **3444**, Determination of mandelic and *p*-bromomandelic acids. **3499**, Determination of Cl^- in organic materials. **3532**, Determination of naphthalene-1:3:6-trisulphonic acid in plating soln. **3764**, Determination of lactose in casein. **3809**, Elementary organic analysis. **3810**, Determination of N. **3851**, Determination of org. compounds by chronopotentiometry.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

3643. **Polarographic methods in clinical chemistry.** M. Březina (Polarographic Inst., Acad. of Sci., Prague). *Acta Chim. Acad. Sci. Hung.*, 1959, **18** (1–4), 69–78 (in German).—Various polarographic methods are discussed, and details are given for the determination of oxygen in blood, the determination of ketosteroids, and the use of the Brdička reaction. (*i*) *Oxygen in blood*—The basal soln. [0·004 *M* $K_4Fe(CN)_6$, 0·05 *M* KCl, 0·05 *M* $Na_2B_4O_7$, 0·1% of saponin and 0·1% of gelatin] is saturated with air, a sample is transferred to the polarographic cell and a layer of liquid paraffin is introduced. The soln. is polarographed from 0·0 V, *vs.* the AgCl electrode, and a known vol. of blood is added from a syringe, with precautions against contamination with air. The soln. is again polarographed after about 5 min. to allow the reaction to take place. A fresh soln. is prepared containing blood, but this time the soln. is aerated before polarographing. From these three results the oxygen content of the blood can be found. (*ii*) *Ketosteroids*—Progesterone is reduced at pH 6 to 7 in aq. ethanol soln. when polarographed from −0·4 V, *vs.* the N.C.E. Deoxycorticosterone can be determined in the presence of methyltestosterone at pH 9·5 in 50% aq. ethanol from −1·2 V, *vs.* the Hg_2SO_4 electrode. The dimethylglycinehydrazone of methyltestosterone can be polarographed at pH 5 in aq. ethanol, from −1·4 V *vs.* the S.C.E. (*iii*) *The Brdička reaction*—This is used in the diagnosis of certain diseases, and is based on the polarography of the filtrate remaining after the pptn. of albumin from serum with sulphosalicylic acid. The compounds responsible for the reducibility of the filtrate have been recognised, namely, a mucoprotein and an albumin which is not pptd. by sulphosalicylic acid. H. M.

3644. **Infra-red spectra of some biochemical substances in water.** F. S. Parker (Dept. of Biochem., State Univ. of New York, Brooklyn, U.S.A.). *Appl. Spectroscopy*, 1958, **12** (6), 163–166.—Infra-red spectra in water can be obtained with the use of a barium fluoride cell in conjunction with a transmittance screen. The use of such spectra to show a chemical change resulting from the dissolution of an unstable compound is illustrated. The solid and solution spectra of α-oxoglutaric acid show typically distinct differences. Spectra for 11 organic acids, including those associated with the citric acid cycle, are given. K. A. PROCTOR

3645. **Determination of potassium in blood serum.** A. E. Teeri and P. G. Sesin (Dept. of Agric. and Biol. Chem., Univ. of New Hampshire, Durham, U.S.A.). *Amer. J. Clin. Path.*, 1958, **29** (1), 86–89.—A buffered 3% soln. of Na tetraphenylboron is added to a suitably diluted protein-free sample of serum and the K is determined by measuring the turbidity at 540 mμ. The method is rapid and simple. Results are in good agreement with those obtained by standard procedures. P. NICHOLLS

3646. **Complexometric determination of calcium in urine.** E. Knappe and V. Böckel (Dtsch. Akad. d. Wissenschaft., Berlin). *Acta Chim. Acad. Sci. Hung.*, 1959, **18** (1–4), 85–91 (in German).—Difficulties previously encountered in the determination of Ca in urine are attributed to the presence of $SO^{2}_{4}{}^{-}$ which can be removed by passing the sample through a cation-exchange medium. The Ca, together with the Mg, is adsorbed and can be removed by washing with 7% HCl soln. The Ca in the eluate is titrated with EDTA soln., with calcein as indicator. This is preferred to murexide or calcon since it gives a sharper end-point and more accurate results. The recommended cation exchanger is Wofatit P, and the pH 2·5 to 3·0. Results are accurate to within ±0·34%. H. M.

3647. **Photometric determination of total calcium in serum and urine.** Yukio Ichinose (Nat. Inst. of Nutrition, Toyama-cho, Shinjuku-ku, Tokyo). *J. Agric. Chem. Soc. Japan*, 1958, **32** (9), 717–719.—Co-pptn. of Mg^{2+} with calcium phosphate is avoided by pptn. of $Mg(OH)_2$ with NaOH. The pptd. calcium phosphate must be washed thoroughly. The P is determined photometrically at 780 mμ with ammonium molybdate and 1-amino-2-naphthol-4-sulphonic acid (**I**). *Procedure*—Mix the sample (0·2 ml) with 50% NaOH soln. (1 ml) and, after 30 min., add Na_2HPO_4 soln. (5%) (0·5 ml) and aq. NH_3 soln. (28%) (4 ml). Set aside overnight and wash the ppt. four times with a mixture

of ethanol, *n*-pentanol, aq. NH_3 soln. (28%) and water (40:3:20:40) containing NH_4Cl (2·6 g per litre); dissolve the ppt. in HCl (1:4) (0·5 ml), mix with $(NH_4)_2MoO_4$ soln. (2·5% in 5 *N* H_2SO_4) (0·5 ml) and **I** soln. (0·25%) (0·5 ml) and dilute to 10 ml for photometry. K. SAITO

3648. **Direct flame-photometric determination of calcium in soil and plant extracts, water and serum with special reference to sodium, potassium and phosphate interference.** M. Puffeles and N. E. Nessim (Div. of Chem. Anal., Min. of Agric., Tel-Aviv, Israel). *Anal. Chim. Acta*, 1959, **20** (1), 38–46.—By using the EEL flame photometer for the determination of Ca, it was found that the presence of Na in the sample caused a large positive error, K a small positive error which became negative with increasing concn., and phosphate a very large negative error. It was therefore concluded that it is possible to determine Ca without prior separation as oxalate in irrigation and drinking water, soil extracts and normal blood sera, but not in plant-ash extracts and abnormal sera.

W. T. CARTER

3649. **Determination of zinc and other elements in plants by atomic-absorption spectroscopy.** D. J. David (Div. of Plant Industry, C.S.I.R.O., Canberra, A.C.T., Australia). *Analyst*, 1958, **83**, 655–661.—A mist of the sample soln. is introduced into a Lundegårdh air - acetylene flame placed between the slit of a flat-field Hilger medium-quartz spectrograph and a hollow-cathode discharge tube emitting intermittent light of the element to be determined at 50 cycles per sec. The plate holder of the spectrograph is replaced by a slit and photomultiplier mounted in guide grooves to align the slit in the focal plane of the spectrograph. This exit slit is placed on the resonance line of the element to be determined, the transmitted light is picked up by the photomultiplier and the amplified rectified signal is measured with a millivoltmeter. The amplifier is adjusted to zero with the slit shutter closed and to full-scale deflection with the shutter open and a mist of water entering the flame. The percentage reduction in the reading when the water is replaced by the sample soln. is a measure of the absorption by the flame of the resonance line of the element. Results are given for Zn, Mg, Cu and Fe determined in plant material. For Zn and Mg the method is as sensitive as other common methods and less subject to interference from other elements. For Cu and Fe it is insufficiently sensitive in its present form. A. O. JONES

3650. **Determination of traces of lead and bismuth in organic material.** J. C. Gage (I.C.I. Ltd., Ind. Hygiene Res. Lab., The Frythe, Welwyn, Herts., England). *Analyst*, 1958, **83**, 672–674.—It is shown that the method previously reported (*Ibid.*, 1955, **80**, 789) for the determination of Pb in organic material is subject to interference by Bi. This can be avoided by reducing to 0·1 *N* the concn. of HCl used to extract Pb from its diethyldithiocarbamate complex in organic soln. Experiments with ashed spinach containing known amounts of Pb and Bi showed that each metal at a concn. of 1 p.p.m. in the fresh spinach can be determined with adequate accuracy in the presence of 100 p.p.m. of the other. Lead and Bi together (each at a concn. of 1 p.p.m.) can be determined in the same soln. by successive extraction with 0·1 *N* and 1·75 *N* HCl with recoveries within 10% of the expected values. Iron (10 p.p.m.) does not interfere with the determination of Bi, but causes slight reduction in the recovery of Pb. A. O. JONES

3651. **Three cases of acute lead poisoning. Analyses of organs for lead and observations on polarographic lead determinations.** O. Karlog and K. O. Møller (Copenhagen Univ., Denmark). *Acta Pharm. Tox., Kbh.*, 1958, **15** (1), 8–16.—After wet-oxidation of the tissue sample, Pb is extracted with dithizone at pH 7·5 in the presence of ammonium citrate, hydroxyammonium chloride, KCN and aq. NH_3. The dithizone is re-extracted with 2 *N* HCl, and Pb is determined polarographically. Calibration is rectilinear up to 200 μg of Pb per ml of final soln. Impurities in the dithizone do not interfere. Values obtained for various organs from three poisoning cases are given. W. H. C. SHAW

3652. **Colorimetric determination of inorganic phosphorus in the presence of glucose 1-phosphate and adenosine triphosphate.** Michinori Nakamura and Kenji Mori (Dept. of Agric. Chem., Univ. of Tokyo, Japan). *Nature*, 1958, **182**, 1441.—The method of Allen (*Biochem. J.*, 1940, **34**, 858) and its modifications have been investigated in respect of the hydrolysis of acid-labile phosphorus compounds during colour development. The amounts of 2:4-diaminophenol hydrochloride and reducing agent and the nature of the acid have some effect on the rate of hydrolysis, but the most important factor is the temp. If colour development is carried out at 18°, very little hydrolysis occurs.

H. F. W. KIRKPATRICK

3653. **Determination of arsenic in biological material.** W. T. Oliver and H. S. Funnell (Dept. of Physiol. Sci., Ontario Vet. Coll., Guelph, Canada). *Anal. Chem.*, 1959, **31** (2), 259–260.—Heat the sample of macerated animal or plant tissue (1 g) with conc. HCl (15 ml) under reflux for 1 hr. Rinse the condenser with H_2O (5 × 10 ml). Cool the combined macerate and rinsings to 25°, add 30% KI soln. (2 ml) and a 40% soln. of $SnCl_2$ in aq. HCl (3 drops), mix and set aside for 15 min. Add 0·1% Tween-80 soln. (1 ml), 2-ethylhexanol (7 or 8 drops) and zinc powder (5 g) and allow the vapours to pass in turn through layers of sand impregnated with Pb acetate, cellulose impregnated with HgI_2 and HgI_2 crystals. After 1 hr., elute the cellulose powder with 0·001 *N* iodine soln. containing 0·01% of sodium alginate (4 × 2 ml). To the eluate add 1% ammonium molybdate reagent (1 ml) and 0·15% hydrazine sulphate soln. (0·4 ml), mix and heat in boiling water for 10 min. Cool rapidly, dilute to 10 ml with H_2O, mix and measure the extinction at 720 mμ against a reagent blank. For samples that contain 20 to 50 μg of As, the coeff. of variation of results is ≃2%; the recovery is almost quantitative. A. R. ROGERS

3654. **Determination of iodine in marine algae and other plant materials.** R. Brühlmann (Kant. Lab., St. Gallen, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (1), 14–17.—The sample is mixed to a paste with K_2CO_3 and water and is then dried and carbonised at 500°. The iodine is extracted, as iodide, from the residue with hot water. Acidified $CHCl_3$ is added followed by $NaNO_2$ to oxidise the I^- to iodine, which is extracted into the $CHCl_3$. The extinction of this soln. is measured at 510 mμ or with suitable colour filters. The accuracy is ≃ ±0·05 mg absolute in the concn. range of 2·5 to 10 mg of iodine. G. P. COOK

3655. **Simple analytical method to determine the proportions of mother and daughter substance in radioactive preparations.** A. Catsch (Inst. für Strahlenbiol. a. d. Reaktor-Sta., Karlsruhe, Germany). *Experientia*, 1958, **14** (9), 345–346 (in German).—A simple and time-saving numerical method is described which permits the rapid determination of mother-to-daughter ratios in biological specimens containing radio-isotopes.
P. NICHOLLS

3656. **Comparison of the results obtained from application of the Hint - Thorsen and anthrone methods for the determination of dextran in blood.** H. Szafranowa, I. Michalska, A. Nowicka and I. Nykowski (Dept. of Pharmacol., Inst. of Pharm., Warsaw). *Acta Polon. Pharm.*, 1959, **16** (1), 35–43.—From results of determinations by both methods, it was found that there was a statistically significant discrepancy. It is concluded that the Hint - Thorsen method (*Acta Chem. Scand.*, 1947, **1**, 808), slightly modified, is more suitable for control determinations of dextran in blood, as it proved to be simpler and easier, and gave more consistent results, than the anthrone method.
W. B. MIASKOWSKI

3657. **Quantitative colorimetric determination of colchicine in aqueous solution, and studies on its application to urine.** E. M. Pearle (Arthritis Clinic, 4th Div. Bellevue Hospital, New York Univ., U.S.A.). *J. Chromatography*, 1959, **2** (1), 108–113.—An attempt to determine colchicine in urine by extraction with 1:2-dichloroethane followed by paper chromatography with benzene - formamide (Burton *et al.*, *J. Biol. Chem.*, 1951, **188**, 763) gave very low recovery although the method was successful with aq. soln. of colchicine. G. BURGER

3658. **Binding affinity of purified plasma proteins for phenylethylbiguanide, an oral hypoglycaemic compound.** H. G. Shepherd, jun., and H. J. McDonald (Dept. of Chem., Grad. Sch., Loyola Univ., Chicago, Ill., U.S.A.). *Clin. Chem.*, 1958, **4** (6), 496–509.—The colorimetric method described for the determination of phenylethylbiguanide is based on the method of Rosenberg *et al.* for the determination of arginine (*Biochem. J.*, 1956, **63**, 153). H. F. W. KIRKPATRICK

3659. **Modification of Malkin's screening test for the detection of artifactually high organic iodine compounds in sera.** M. Barker and E. B. Man (Yale Univ. Med. Sch., New Haven, Conn., U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (4), 659–660.—Improved sensitivity in the test (*cf.* Malkin, *Anal. Abstr.*, 1957, **4**, 223) is attained by substituting 0·5 ml of aq. KI soln. (1·4 mg in 100 ml) for 0·5 ml of water. The addition of 2 drops of 27 *N* H_2SO_4 after the digestion with KOH enables the ceric and arsenite reagents for the butanol-extractable iodine test to be used for both tests. W. H. C. SHAW

3660. **Spectrophotometric method for the determination of Evans blue dye in the presence of haemolysis and turbidity.** L. H. Hamilton (Marquette Univ. Med. Sch., Milwaukee, Wis., U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (5), 762–767.—Interference in the determination of Evans blue (azovan blue) in plasma by haemoglobin with or without additional turbidity (fat) may be eliminated by the method described. With the spectrophotometer used, the equation E_{625} (corr.) = E_{625} (obs.) — 1·793 E_{745} was found to be correct within an E value of 0·003 for 22 determinations in plasma or serum samples with interference of the two types.
W. H. C. SHAW

3661. **Simple rapid and accurate method of extracting T-1824 [azovan blue] from plasma adapted to the routine measurement of blood volume.** T. J. Campbell, B. Frohman and E. B. Reeve (Colorado Univ. Med. Sch., Denver, U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (5), 768–777.—In the method described, the dye is displaced from combination with albumin in the sample with Teepol in phosphate soln. The mixture is then passed through a column of wood cellulose (Solka Floc SW-40-A) on which the dye is adsorbed and interfering substances are eluted with 2% aq. Na_2HPO_4 soln. The dye is then eluted with acetone - water (1:1) adjusted to pH 8·0 with *N* NaOH, and the extinction is measured at 615 mμ after adjustment of the pH to 6·8 with KH_2PO_4. The observed results may be related to "normal" blood volume by the nomogram given. W. H. C. SHAW

3662. **Micro-determination of acetone in biological fluids.** M. U. Tsao, G. H. Lowrey and E. J. Graham (Dept. of Pediatrics and Communicable Diseases, Univ. of Michigan Med. Sch., Ann Arbor, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 311–314.—Heat 2:4-dinitrophenylhydrazine (10 mg) with a mixture of conc. H_2SO_4 (0·05 ml) and 95% ethanol (10 ml) at 50° until most has dissolved, and cool. Pipette 150 μl of this soln. into an absorptiometer tube, the lower part of which is immersed in ice water and the upper part maintained at about 38°. Place a 10-μl aliquot of the sample on filter-paper (8 mm × 16 mm) supported within the tube and allow diffusion to proceed for 90 min. Remove the tube, and after a further 30 min. at room temp. add 9 *N* NaOH (0·3 ml). Mix and set aside for 30 min. Add 50% ethanol (3 ml) and measure the extinction at 540 mμ, 15 min. after the addition of the alcohol. A correction may be applied for interference caused by acetaldehyde. The limits of error ($P = 0·95$) for the recovery of 5 μg of acetone from samples of blood and urine are 1·5% and 1·2%, respectively.
A. R. ROGERS

3663. **Enzymatic method for glucose determination in body fluids.** E. F. Beach and J. J. Turner (Biochem. Lab., Met. Life Ins. Co., New York, U.S.A.). *Clin. Chem.*, 1958, **4** (6), 462–475.—Glucose oxidase - peroxidase from horseradish root (preparation described), and *o*-anisidine as colour reagent, are used in the method described, which is applied to the qual. detection of glucose in urine, and its quant. determination in urine and blood.
H. F. W. KIRKPATRICK

3664. **Reaction between *meso*inositol and uranyl acetate.** P. Meredith and H. G. Sammons (Dept. of Med. Biochem. and Pharmacol., Univ., Birmingham, England). *Analyst*, 1958, **83**, 686.—A reaction between *meso*inositol and uranyl acetate soln. may serve as a method of detection of *meso*-inositol on paper chromatograms and of its determination in soln. after chromatographic separation of other polyols. The chromatogram is lightly sprayed with a 2% aq. soln. of uranyl acetate and is immediately examined under u.v. light. A green fluorescence indicates the presence of inositol. In aq. soln. (pH 4·4) the large blank fluorescence of uranyl acetate is only feebly enhanced by inositol. When increasing amounts of NaOH are added, the

increase in fluorescence caused by inositol is decreased to the point where the effect of inositol is reversed and quenching occurs, and this quenching effect, being greater than the enhancement, is more suitable for measurement. A tentative method is described in which the quenching effect is used for the determination of inositol eluted from paper chromatograms. Standard graphs are reproducible in the range 20 to 200 μg. The absorption graph of the yellow complex formed by inositol and uranyl acetate has peaks at 356, 315 and 240 mμ, but the sensitivity attained does not approach that of the quenching method. A. O. JONES

3665. **Biochemical aspects of bovine ketosis. [Micro-determination of pyruvate, citrate, α-oxoglutarate and succinate.]** S. J. Bach and K. G. Hibbitt (Dept. of Physiol., Univ. of Bristol, England). *Biochem. J.*, 1959, **72** (1), 87–92.—Standard micro-methods are adapted for the determination of 1 to 2 μg of pyruvate, citrate and α-oxoglutarate in serum, and a new method is described for the determination of succinic acid. Pyruvate and α-oxoglutarate are determined by modifications of the dinitrophenylhydrazone method, and citrate by the pentabromoacetone method. Succinic acid is extracted with diethyl ether from serum deproteinised with tungstic acid. After evaporation of the ether, the residue is dissolved in phosphate buffer, pH 7·6, and the enzymic (succinoxidase) reduction of cytochrome *C* by succinic acid in the presence and absence of malonate is determined spectrophotometrically at 550 mμ. J. N. ASHLEY

3666. **Chromatographic separation of pyruvic, oxalacetic and α-oxoglutaric acid from tissue cultures.** G. A. Abdel-Tawab, E. Broda and G. Kellner (Univ., Vienna). *J. Chromatography*, 1959, **2** (1), 99–107.—These acids have been separated by descending chromatography of their 2:4-dinitrophenylhydrazones on filter-paper freshly impregnated with 0·1 *M* phosphate buffer (pH 7·4), with *n*-butanol - 3% aq. NH_3 (1:1) as solvent. The pyruvic acid derivative gives two spots when the acid is extracted from a tissue culture, and the derivatives of oxalacetic and α-oxoglutaric acids one each. The oxalacetic acid derivative is decomposed to the pyruvic acid derivative by moderate heat, so that exposure to heat during analysis should be avoided. The bands were extracted with buffer soln. and the concn. determined colorimetrically. As this analysis formed part of an investigation with radio-tracers, the activity of the bands was determined with a CO_2-filled Geiger counter. The derivatives were formed in the deproteinised culture medium and extracted with ether; 2 μg of the acids can be determined. G. BURGER

3667. **Formation of indol-3-ylacetic acid and tryptamine in animals. Method for estimation of indol-3-ylacetic acid in tissues.** H. Weissbach, W. King, A. Sjoerdsma and S. Udenfriend (Lab. of Clin. Biochem., Nat. Heart Inst., Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1959, **234** (1), 81–86.—A sensitive and specific method is described for the determination of indol-3-ylacetic acid (**I**) in urine and tissues. It is based on a modified xanthhydrol reaction as described for the determination of tryptophan by Dickman and Crockett (*Anal. Abstr.*, 1956, **3**, 3721). The urine is extracted with aq. HCl - $CHCl_3$, and the $CHCl_3$ layer is extracted with phosphate buffer (pH 7·0). An aliquot of the buffer soln. is treated with HCl, xanthhydrol and $NaHSO_2$ and after 5 to 10 min. the extinction of the pink colour is measured spectrophotometrically at 520 mμ. For 8 to 200 μg of **I**, the extinction is proportional to concn. With extracts of tissues, increased sensitivity is needed, and this is obtained by a fluorimetric assay after pptn. of proteins. J. N. ASHLEY

3668. **Concentration of vitamin B_{12} from urine by adsorption on carbon.** C. H. Buchholz (Veterans Admin. Hosp., Long Beach, Calif., U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (4), 653–656.—Increased sensitivity in the assay of radio-cyanocobalamin is attained by adsorption from the acidified sample on to activated carbon, which is then counted in a well-type scintillation counter. By this method a Schilling test may be carried out with a test dose of 0·05 μC. W. H. C. SHAW

3669. **Determination of bilirubin in serum as alkaline "azobilirubin".** J. Fog (Med. Dept. B, Univ. Clinic, Oslo City Hospital, Norway). *Scand. J. Clin. Lab. Invest.*, 1958, **10** (3), 241–245.—The method of Jendrassik and Gróf (*Biochem. Z.*, 1938, **297**, 81) is adapted for use with a spectrophotometer. The van den Bergh reaction with diazotised sulphanilic acid is carried out on 1 ml of serum in the presence of caffeine - sodium benzoate accelerator. After making the soln. alkaline, the absorption is measured at 600 mμ. At this wavelength the absorption of the yellow non-bilirubin pigments of serum, and of pigments preformed or arising in the reaction, is negligible. Beer's law is obeyed over a wide range of bilirubin concn., and the method is specific and accurate. D. W. MOSS

3670. **Paper-chromatographic separation of the coproporphyrin isomers I and III.** L. Eriksen (Inst. Med. Biochem. and Physiol., Univ., Oslo, Norway). *Scand. J. Clin. Lab. Invest.*, 1958, **10** (3), 319–321.—The separation is performed by a modification of an earlier column method (*Ibid.*, 1957, **9**, 97), which depends on the number of acid groups in the porphyrin molecule. The mixture of compounds is dissolved in 10% aq. NH_3 - acetone (3:10), and is spotted on Whatman No. 1 paper, which is then developed by ascending chromatography with 2:6-lutidine - water in an atmosphere of ammonia. No temp. control is necessary, but light should be excluded. The method is simple and reliable. D. B. PALMER

3671. **Accumulation of acetylmethylcarbinol and acetylethylcarbinol by a mutant of *Neurospora crassa* and its significance in the biosynthesis of *iso*leucine and valine. [Determination of acetylmethylcarbinol and acetylethylcarbinol.]** R. P. Wagner, A. Bergquist and H. S. Forrest (Genetics Lab., Dept. of Zool., Univ. of Texas, Austin, U.S.A.). *J. Biol. Chem.*, 1959, **234** (1), 99–104.—The method is based on the condensation of each carbinol with 2:4:5-triamino-6-hydroxypyrimidine to give the corresponding pteridines. The condensation products are dissolved in 1% aq. NH_3 and chromatographed on paper in 1% aq. NH_3 in *n*-propanol. The two fluorescent bands are cut out, the material from each is eluted with 1% aq. NH_3, and the amounts of each pteridine are ascertained from the extinctions at 355 mμ of each eluate in 0·1 *N* NaOH. J. N. ASHLEY

3672. **Chromatographic identification and determination of xylose and arabinose in the pentosans of soya bean.** A. Troparevsky, A. E. A. Mitta and

M. L. Pisarello (Dept. of Biol. Chem., Univ., Buenos Aires). *An. Asoc. Quim. Argentina*, 1958, **46** (3), 253–257.—The xylose and arabinose contents of soya bean (variety CNS 24 from S. Carolina), determined colorimetrically after paper-chromatographic separation of the sugars, were 0·35% and 3%, respectively; 0·91% of another pentose, presumably ribose, was also present. Satisfactory separation of both xylose and arabinose from hexose sugars was not obtained on the same chromatogram and, for the determination, xylose was separated by using ethyl acetate - pyridine - water - acetone (2:1:1:1), and arabinose by using phenol - water. An extract of the defatted soya bean was prepared by heating under reflux for 1 hr. with 6·5 ml of HCl (d = 1·125) and 65 ml of water, defecating with 15 ml of 10% Na_2WO_4 and diluting to 100 ml. For the elimination of salts, a 5-ml aliquot was evaporated to dryness on the water bath, treated with 5 ml of dry pyridine at 100° for 10 min., cooled and filtered. The pyridine soln. was evaporated at $<40°$ and the residue dissolved in 2·5 ml of water. The sugars were separated by ascending chromatography on Whatman No. 1 paper, eluted, and determined colorimetrically by the method of Dubois (*Nature*, 1951, **168**, 167). E. C. Apling

3673. **Detection of pollen flavonoids by fluorescence on impregnated papers.** G. E. Inglett, R. R. Miller and J. P. Lodge (Dept. of Health, Educ. and Welfare, Public Health Service, R. A. Taft San. Engng Center, Cincinnati, Ohio, U.S.A.). *Mikrochim. Acta*, 1959, (1), 95–100 (in English).—Strips are prepared by dipping Whatman No. 4 paper into 0·1% aq. soln. of $ZrOCl_2.8H_2O$, $AlCl_3.6H_2O$ or $BeSO_4$ (this soln. adjusted to pH 11), and allowing to dry in air. Many flavonoid glycosides and related compounds, applied as 0·01% ethanolic soln. and allowed to dry in air, form chelate compounds which fluoresce under u.v. light. In many cases the colour and intensity of the fluorescence differs according to the strip, permitting qual. identification. Results are presented for 34 substances and it is shown that orchard-grass pollen-extract contains dactylin and *iso*quercetin, while timothy-grass pollen-extract contains only dactylin. Limits of identification are listed for 21 compounds giving an observable spot. T. R. Andrew

3674. **Specific colour reaction for rutin.** Shozo Kamiya (Nat. Hygienic Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *Japan Analyst*, 1958, **7** (11), 717–718.—On application of the modified indophenol method for the detection of phenols (Itai and Kamiya, *Anal. Abstr.*, 1959, **6**, 3590), rutin (>2 μg) changes at first to blue then to green. The colour fades on the addition of NaClO (0·02% aq. soln., 2 drops). Among related compounds, hesperidin (>10 μg), hesperetin (>2 μg) and acacetin (>5 μg) give a similar coloration which becomes more intense on addition of NaClO.

K. Saito

3675. **Method for determining monosaccharides and uronic acids in wood hydrolysates.** O. Perilä and T. Seppä (Lab. of Wood Chem., Inst. of Technol., Helsinki, Finland). *Suomen Kem., B*, 1958, **31** (12), 383–384.—This method makes it possible to determine monosaccharides and uronic acids by paper chromatography without previous fractionation of the components by other methods. After total hydrolysis of the wood with H_2SO_4 soln. the resulting sugar soln. is neutralised with $BaCO_3$, filtered, and concentrated. Whatman No. 1 paper saturated with 0·05 N $Ba(OH)_2$ is employed. When using neutral solvents, *e.g.*, ethyl methyl ketone - acetone - water (15:5:3), the monosaccharides are separated in the normal manner, but the uronic acids move only a short distance. The monosaccharides are determined by the method of Matzusaki and Ward (*TAPPI*, 1957, **40**, 650). When the uronic acids are also to be determined, only one edge of the paper, used as a stationary phase, is treated with $Ba(OH)_2$ soln. After elution with a neutral solvent as described above, the paper strip is dried, and the uronic acids are separated in the crosswise direction with an acid solvent, *e.g.*, ethyl acetate - acetic acid - formic acid - water (18:3:1:4). E. Sjöström

3676. **Studies on tannins. VII. Colorimetric determination of (+)-catechin in catechu.** Koiti Kimura, Yukishige Satomi and Shigeaki Kuwano (Pharm. Fac., Osaka Univ., Hotarugaike, Toyonaka). *J. Pharm. Soc. Japan*, 1958, **78** (4), 325–329.—The colorimetric method of Mayer for the determination of (+)-catechin (**I**) with vanillin in HCl (*Leder*, 1956, **7**, 33) was applied, with some modifications, to the analysis of Gambier catechu. For the paper-chromatographic separation of **I** from Gambier tannin (**II**), a mixture of benzene, propanol, acetic acid and water (4:2:1:1, by vol.) is preferred (R_F for **I**, 0·25; for **II**, $\simeq 0$). The sample (1 g) is extracted with methanol in a Soxhlet apparatus, the extract is diluted to 50 ml and one drop is chromatographed. The spot of **I** is cut out, dried *in vacuo* at 90° for 6 hr., extracted with methanol (2 ml), mixed with vanillin in methanolic HCl (3 vol. of 10% vanillin in methanol and 1 vol. of 35% HCl) (5 ml) and the extinction is measured at 500 mμ after 15 min. K. Saito

3677. **Studies on wasabi. IV. Determination of sinigrin.** Zenji Nagashima, Masaaki Uchiyama and Yasushi Utsugi (Fac. of Agric., Shizuoka Univ., Mishima). *J. Agric. Chem. Soc. Japan*, 1958, **32** (7), 521–525.—Sinigrin (**I**) is separated with Amberlite LR-4B (Cl), with 0·2% KOH soln. as eluting agent (Nagashima, *Ibid.*, 1957, **31**, 514), and is then determined by its quant. reduction of $K_3Fe(CN)_6$ in alkaline soln. *Procedure*—Crush wasabi root (0·5 g) with methanol (70%, 5 ml) and sand, dilute with methanol (70%, 10 ml) and centrifuge. Repeat the extraction. Pass a 5-ml portion of the methanolic soln. through a column of resin (diam., 6 mm; vol. of resin, 0·7 ml; rate of flow, 0·1 ml per min.), wash with water (40 ml) and elute **I** with 0·2% KOH soln. (0·2 ml per min., 50 ml). Heat a 5-ml portion of the eluate with aq. $K_3Fe(CN)_6$ soln. (1·650 g per litre containing 10·6 g of Na_2CO_3) (2 ml) in a water bath for 15 min. and titrate the excess of $K_3Fe(CN)_6$ soln. iodimetrically.

K. Saito

3678. **Electrophoretic analysis of plant-virus preparations.** P. M. Townsley (Chem. Div., Canad. Dept. of Agric., Vancouver, B.C.). *Canad. J. Biochem. Physiol.*, 1959, **37** (1), 119–126.—Tri-(hydroxymethyl)methylamine maleate buffer (pH 7·0), with 0·7% agar and a final buffer molarity of 0·02, is used. Leaf juice is expressed at 0° and applied immediately to the origin. Electrophoresis is carried out with a p.d. of 150 V and a current of 14 mA. The location of tomato mosaic virus and potato virus X is effected by autoradiography, serological and protein-staining methods.

H. F. W. Kirkpatrick

3679. **Paper-chromatographic determination of creatine phosphate and orthophosphate in tissue extracts.** E. Gerlach and J. Janke (Inst. of Physiol., Univ. of Freiburg). *Biochem. Z.*, 1958, **330** (7), 565–575.—A new solvent system is described for use in the two-dimensional chromatographic separation of creatine phosphate (**I**) and orthophosphate (**II**) from each other and from other phosphorus compounds. This solvent consists of methanol - *iso*propyl alcohol - 25% aq. NH_3 - H_2O (9:6:3:2), which is used for the first run, followed by di*iso*propyl ether - *n*-butanol - formic acid (98%) (4:3:2). The method used is that of Gerlach *et al.* (*Naunyn-Schmiedebergs' Arch. exp. Path. Pharmak.*, 1955, **226**, 9). The R_F values of 28 phosphorus-containing compounds are given, that of **I** being 1·00, and that of **II** being 0·52. Recoveries of 96·5% to 99·5% were obtained. This new solvent is applied to the determination of **I** and **II** in various rat organs and tissues. The organs and tissues are frozen *in situ*, removed, and extracted with ice-cold $HClO_4$. Interfering ions are removed by treating the extract with a soln. of EDTA. Following neutralisation of the soln. and removal of the pptd. $KClO_4$, aliquots are taken for chromatography. The developed chromatogram is sprayed with a molybdate reagent, and the revealed phosphorus compounds are determined by the method of Berenblum and Chain (*Biochem. J.*, 1938, **32**, 295). Results are reported for the content of **I** and **II** of skeletal muscle, heart muscle, brain, intestinal mucosa, kidney and liver, and the levels quoted are affected significantly by the technique of tissue isolation. The possibility of using this method in studies with ^{32}P is discussed.

D. B. PALMER

3680. **Paper-chromatographic determination of creatine phosphate.** B. E. Wahler (Arbeitsstelle f. Kreislaufforsch. der Dtsch. Akad. der Wissenschaften zu Berlin, Arbeitsgruppe f. Biochem., Berlin-Buch). *Naturwissenschaften*, 1959, **46** (1), 16.—A quant. determination of orthophosphate and creatine phosphate or phosphoglycocyamine in the presence of each other is obtained by the paper chromatography of a weakly acid extract (pH 5 to 7). Data are tabulated of R_F values and identifying reactions for the constituents of heart and brain muscle. A special procedure is described for the determination of molybdate-labile N-phosphono acids.

J. L. PROSSER

3681. **Identification of histamine, N-dimethylhistamine, N-acetylhistamine and acetylcholine in *Spinacia oleracea*.** W. Appel and E. Werle (Wissenschaft. Lab. der Chirurg. Klinik, Univ., München). *Arzneimittel-Forsch.*, 1959, **9** (1), 22–26.—Extracts of spinach were prepared with the following reagents —methanol, water, 0·1 *N* HCl and basic Pb acetate soln. Each extract was subjected to ion-exchange chromatography. The iminazole derivatives contained in individual fractions were examined and identified by paper chromatography and tested pharmacologically by studying their effect on the blood pressure of dogs. The main iminazole derivatives were histamine and N-acetylhistamine. The presence of the latter was suspected when much acetylcholine was found. Small amounts of dimethyl- and traces of trimethylhistamine were also present. In addition to paper-chromatographic and pharmacological studies of various components, total iminazole derivatives were determined by the diazo reaction.

M. H. SAWISTOWSKA

3682. **Colour tests and determination of noradrenalone hydrochloride in non-aqueous medium in the presence of adrenalone hydrochloride.** I. Gyenes, A. Mizsei and L. Szagó (Anal. Dept., Gedeon Richter A.-G., Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **16** (4), 389–402 (in English).—A satisfactory quant. test is described. Dissolve 93 to 97 mg of sample in pure pyridine and dilute the soln. to 50 ml with solvent. To 1 ml add 5 ml of reagent [4% (w/v) $HgCl_2$ in pyridine], shake, stopper the tube and set aside for 1 hr. at 25°. Measure the extinction at 353 mμ in a 1-cm cell. This test will detect 0·003 to 0·03 mg of noradrenalone hydrochloride (**I**) in the presence of 2 mg of adrenalone hydrochloride (**II**). A qual. test consists in adding 4% (w/v) Pb acetate trihydrate in dimethylformamide (5 ml) to a soln. of 10 mg of **I** in the same solvent (1 ml), when the presence of 0·02 mg of **II** is shown by the formation of a ppt. with a distinct greenish-blue tint.

H. F. W. KIRKPATRICK

3683. **Determination of uridine and thymine in small samples of nucleic acid protein residue.** K. F. Jervell, C. R. Diniz and G. C. Mueller (Wisconsin Univ. Med. Sch., Madison, U.S.A.). *Arch. Biochem. Biophys.*, 1958, **78** (1), 157–164.—The sample is hydrolysed under controlled conditions with 98% formic acid, and the hydrolysate is then purified by passage through a column of prepared Dowex ion-exchange resins. The first fraction obtained with 0·01 *N* HCl contains uridine, uracil and thymine which, after evaporation of the HCl, are chromatographed by the descending technique on Whatman No. 52 paper with water-saturated *n*-butanol. After development, appropriate areas, identified under u.v. light, are cut out and eluted with 0·01 *N* HCl, and individual compounds are then determined from the extinctions of the eluates. The procedure is applicable to isotopically labelled nucleic acids.

W. H. C. SHAW

3684. **Quantitative determination of xanthurenic acid in urine.** R. H. H. Richter (Frauenklinik, Univ., Bern, Switzerland). *Chimia*, 1958, **12** (11), 328.—To assure quant. recovery of xanthurenic acid (100 to 500 μg) from urine (4 ml) with $(NH_4)_2SO_4.Fe_2(SO_4)_3$ reagent, it is essential to run recovery checks, since some literature procedures give variable recoveries. Citric acid, salicylic acid, ascorbic acid and EDTA interfere. The urine must be at pH 6 to 8 before the addition of buffer, and should be sampled when subjects are not receiving medication.

J. P. STERN

3685. **Isolation, detection and measurement of microgram quantities of labelled tissue nucleotides.** K. K. Tsuboi and T. D. Price (Cornell Univ. Med. Coll., New York, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **81** (1), 223–237.—The preliminary separation of labelled nucleotide mixtures, obtained from tissue samples after the administration of ^{32}P, from non-nucleotide activity is attained by adsorption on activated charcoal (Norit A). After separation and washing, the nucleotides are eluted from the charcoal and individual components are then separated by two-dimensional paper chromatography. The compounds are located by radioautography and by photography under u.v. light. The reactions of Norit A with purine and pyrimidine compounds in general, their chromatographic behaviour with different solvent systems, and the identification and specific activity of the isolated nucleotides of rat organs are discussed.

W. H. C. SHAW

3686. **Estimation of pentose- and deoxypentose-nucleic acids in ox liver.** S. K. Dutta (Bengal Immunity Res. Inst., Calcutta). *Indian J. Pharm.*, 1959, **21** (1), 8–12.—To separate pentosenucleic acid (**I**) and deoxypentosenucleic acid (**II**) from the mixture of nucleic acids, the method of Dutta *et al.* (*cf. Brit. Abstr. C*, 1953, 359) is used. By hydrolysis of the isolated **I** and **II** with 60% $HClO_4$ at 100° for 1 hr., and chromatography of an aliquot of the neutralised hydrolysate with *n*-butanol - pyridine - water (6:4:3), separation of the constituent purines and pyrimidines is obtained. These are determined spectrophotometrically after location by u.v. photography (Markham and Smith, *Biochem. J.*, 1949, **45**, 294), and elution with 0·1 *N* HCl at 37° for 16 hr. A further aliquot of the hydrolysate is analysed for N and P by a micro-method (Jones *et al.*, *J. Chem. Soc.*, 1951, 623). The number of moles of the bases per 100 g-atoms of P can then be calculated, and by determining the molar concn. of uracil and thymine per 100 g-atoms of P the amounts of **I** and **II** originally present can be calculated. For the determination of **I** and **II** in ox liver, the samples are homogenised, treated with ice-cold 1% $HClO_4$, and the ppt. is washed with 0·5% $HClO_4$, ethanol, and diethyl ether. The dry material is then extracted twice with 6% $HClO_4$ at 80° for 30 min., the extracts are combined, and concentrated at 100° for 60 min. After neutralisation, the soln. is passed through a column of Zeo-Karb 215 (hydrogen form), then through a column of Decolorite, and the percolate is concentrated and analysed chromatographically as previously described. From the uracil and thymine content the original amounts of **I** and **II** are calculated. Results obtained by this method are compared with those from two other methods which are based on (*i*) determination of P, and (*ii*) determination of the sugar moiety. With pure **I** and **II** the results from the present method agree only with those by method (*ii*), but with samples of ox liver the results by all 3 methods differed. Possible reasons for this are discussed. D. B. PALMER

3687. **Gas-chromatographic investigation of the nitrometer gases resulting from Van Slyke amino-group determinations.** G. Kainz and H. Huber (II Chem. Inst., Univ., Vienna). *Mikrochim. Acta*, 1959, (1), 51–60.—Thirty-seven organic compounds, including many that have been observed to give high values for amino nitrogen, have been treated by the Van Slyke method and the nitrometer gases examined by gas chromatography. With the exception of uric acid, which yielded pure N, all the compounds studied gave mixtures of N and N_2O in proportions which were affected by substituents. It is suggested that the presence of N_2O is indicative of anomalous high values. T. R. ANDREW

3688. **Qualitative aldehyde reactions. Identification of amino acids.** R. W. Storherr (Georgia Exp. Station, Experiment, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 268–270.—Reactions between aldehydes and amino acids in glacial acetic acid provide a new means for the identification of specific amino acids. Furfuraldehyde reacts with most common amino acids producing a common absorbance maximum in the range 360 to 380 mμ. The lysines and ornithine exhibit a second peak at 515 to 530 mμ which is specific for this group of diamino acids. *sym.*-Trioxan reacts specifically with hydroxyproline giving a maximum at 492 to 494 mμ. Only milligram amounts of original protein are required for the identifications. G. P. COOK

3689. **Chromatography of dipolar ions. Activity coefficients of amino acids and peptides in ion-exchange resins.** J. Feitelson (Hebrew Univ., Jerusalem, Israel). *Arch. Biochem. Biophys.*, 1959, **79**, 177–186.—A study is made of the distribution of glycine, alanine and leucine and their simple peptides on Dowex-50 ion-exchange resin (4% cross-linked) at different pH values of eluent buffer and constant Na^+ concn. The equilibria involved in chromatography, the distribution and activity coefficients and the factors governing resin - solute interaction are discussed. W. H. C. SHAW

3690. **Rapid paper-chromatographic procedure for the quantitative determination of hydroxyproline.** H. R. Roberts, M. G. Kolor and W. Bucek (Nat. Dairy Products Corp., Oakdale, Long Island, N.Y., U.S.A.). *Nature*, 1958, **182**, 1602.—Modification of a previously described method (Roberts and Kolor, *Nature*, 1958, **181**, 837) reduces the time of development from 40 hr. to 4 hr. Horizontal chromatography replaces descending chromatography and development at a higher temp. is carried out in an oven at 60°. H. F. W. KIRKPATRICK

3691. **The Sakaguchi reaction of arginine on filter-paper.** K. R. Bhattacharya, J. Datta and D. K. Roy (Indian Inst. for Biochem., Calcutta). *Arch. Biochem. Biophys.*, 1958, **77** (2), 297–311.—The effects of different concn. of 1-naphthol, arginine, hypobromite, urea and alkali, and of temp., on the colour developed in the reaction are studied. The mechanism of the reaction is discussed in relation to the results obtained, and a procedure for the determination of arginine on paper chromatograms is given. W. H. C. SHAW

3692. **Spectrophotometric determination of arginine by the Sakaguchi reaction.** Kazuo Satake and J. M. Luck (Dept. of Chem., Stanford Univ., Calif., U.S.A.). *Bull. Soc. Chim. Biol.*, 1958, **40** (12), 1743–1756 (in English).—A method similar to that of Szilágyi and Szabó (*cf. Anal. Abstr.*, 1958, **5**, 3122), but with 8-hydroxyquinoline instead of 1-naphthol, is described. The test soln. (1 to 25 μg of arginine per ml) (2 ml) is mixed with 2 ml of 0·02% 8-hydroxyquinoline in 3 *N* NaOH, followed by 1 ml of 0·1% N-bromosuccinimide, added with shaking. After 5 to 30 min. the extinction is read at 500 mμ against water as blank. Hydrolysates containing inhibitory concn. of other amino acids are dinitrophenylated by the method of Porter and Sanger (*Biochem. J.*, 1948, **42**, 287), and interfering amino acids are removed by extraction with diethyl ether. Dinitrophenol arginine in 0·1 *N* HCl is used as a standard. Alternatively, untreated hydrolysate may be determined, with 1 ml of hydrolysate plus 1 ml of standard arginine soln. as a working standard. D. G. Moss

3693. **New colour reaction for tryptophan or tryptophan-containing proteins.** R. L. Searcy (Los Angeles County Osteopathic Hosp., Calif., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **81** (1), 275–276.—The method is based on the development of a purple colour when tryptophan, or proteins containing it, are treated with toluene-*p*-sulphonic acid. Calibration is rectilinear with up to 4·0 mg of serum of known globulin concn., serum total globulins or serum γ-globulins. *Procedure*—To 0·1 to 4·0 mg of protein fractions add 10·0 ml of 12% toluene-*p*-sulphonic acid in glacial acetic acid. Heat at 100° for 15 min., cool and read the extinction against a reagent blank at 560 mμ. W. H. C. SHAW

3694. **Methods for the qualitative, semi-quantitative and quantitative determination of iodoamino acids and of inorganic iodide in iodoprotein digests and in human serum.** R. H. Mandl and R. J. Block (Boyce Thompson Inst. Inc., Yonkers, N.Y., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **81** (1), 25–35.—The method described is suitable for serum and iodoprotein digests obtained after the administration of ^{127}I. After incubation with pancreatin, the iodoamino acids are concentrated by extraction into *n*-butanol and then submitted to chromatography on cellulose powder and developed with *iso*butyl alcohol - 3% w/v aq. NH_3 (3:1). This treatment separates thyroxine, 3:5:3′-tri-iodothyronine and other iodothyronines from mono- and di-iodotyrosine, I^-, and other amino acids. The two fractions are concentrated, and then re-chromatographed on Whatman No. 3 paper by the descending technique for 24 hr. with the above solvent. The concn. of the compounds may be estimated visually by comparison with known standards after treatment with a $Ce(SO_4)_2$ - arsenite reagent, followed by counter-staining with methylene blue (sensitivity 0·1 μg of organic iodine). For quant. purposes the spots are cut out and eluted, and the compounds determined with the ceric - arsenite reagent either visually or, for improved reproducibility, with a recording colorimeter (sensitivity 0·005 μg of organic iodine). Discrepancies between results for thyroxine and biological activity are discussed. W. H. C. SHAW

3695. **Zone electrophoresis of cerebrospinal fluid in starch gel.** J. H. Pert and H. Kutt (Neurolog. Service, Bellevue Hosp., Cornell Univ. Med. Coll., N.Y., U.S.A.). *Proc. Soc. Exp. Biol. Med.*, 1958, **99** (1), 181–185.—A method for the separation of cerebrospinal fluid proteins is presented and its value discussed. A technique for staining lyoproteins in cerebrospinal fluid and serum is described. B. P. BLOCK

3696. **Technique for separation of protein by means of agar-gel electrophoresis.** B. Zak and K. M. Sun (Dept. Path., Wayne State Univ. Coll. of Med., Detroit, Mich., U.S.A.). *Amer. J. Clin. Path.*, 1958, **29** (1), 69–79.—A simple method is described for the preparation of electropherograms on dil. agar in barbitone buffer (pH 8·6) supported on glass plates. After electrophoresis, the plates are dried and stained by the conventional reagents. The dried stained plate is then treated with immersion oil and covered with another glass plate to obtain increased clarity of the background. The extinctions of the stained zones are measured at 610 mμ in a densitometer. This procedure precludes artefacts resulting from scattering of light by fibres that are normally encountered in paper electrophoresis. The technique has been applied to the separation, identification and quant. determination of proteins in serum and cerebrospinal fluid and of abnormal haemoglobins. P. NICHOLLS

3697. **Determination of free protein mobilities by paper electrophoresis with evaporation. I. Evaluation of the buffer flow due to evaporation and electro-osmosis.** K. Schilling and H. Waldmann-Meyer (Biol. Inst., Carlsberg Found., Copenhagen, Denmark). *Acta Chem. Scand.*, 1959, **13** (1), 1–12 (in English).—Paper strips resting on nylon threads between glass plates 6 mm apart were used, and the current passed was kept constant. A linear relation was found between the migration distance of a dextran spot and the distance from the starting point to the strip centre, provided that experiments were confined to the region of uniform buffer concn. in the centre portion of the strip. Equations are given for calculating the evaporation and electro-osmosis parameters. Being constant for a given current, these need not be evaluated if dextran and protein spots are run under identical conditions, as the difference in migration distance equals $mV_t t$, where m = protein mobility on the paper, V_t = voltage at time t when migration is stopped. The R_F of dextran in the buffer used was $\simeq 1$, and its electrophoretic mobility negligible.

II. Evaluation of temperature and concentration increases, influence of the carrier medium, and measurement of serum-protein mobilities. H. Waldmann-Meyer and K. Schilling. *Ibid.*, 1959, **13** (1), 13–28.—Protein mobilities in free soln. may be calculated from electrophoresis data by correcting for (*i*) protein adsorption, (*ii*) path-length increase due to paper structure, (*iii*) salt concn. in the migration zone and (*iv*) temp. increase on the strip. (*i*) is evaluated by running a protein and a dextran spot at each end of the paper, each pair at a different distance from the centre. The adsorption factor is $Sp_1 - Sp_2/Sd_1 - Sd_2$, where Sp and Sd are the migration distances for protein and dextran, respectively. It varies with buffer concn.; (*ii*) is obtained by comparing the conductivities of moist paper and an equivalent buffer column, and is constant for a given brand of paper; (*iii*) is a function of the input of watts, and must be found for the apparatus used; (*iv*) is calculated from the "dextran shrinkage" (the distance between starting positions divided by the distance between final positions). Free mobilities of serum albumin and γ-globulin calculated from the final equation agreed excellently with moving boundary data. D. G. MOSS

3698. **New method for starch-gel electrophoresis of human haemoglobins, with special reference to the determination of haemoglobin A_2.** C. A. J. Goldberg (William Pepper Lab. of Clin. Med., Univ. of Pennsylvania, Philadelphia, U.S.A.). *Clin. Chem.*, 1958, **4** (6), 484–495.—The method differs from that previously described (Goldberg, *Scand. Clin. Lab. Invest.*, 1957, **10** (suppl. 31), 273) in the use of a discontinuous buffer system. The starch bed is made with buffer soln. (pH 9·0) composed of tri(hydroxymethyl)methylamine (6·05 g), disodium EDTA dihydrate (0·780 g) and H_3BO_3 (0·460 g) dissolved in water and the vol. made up to 2 litres. Barbitone buffer soln. (0·06 *M*) (pH 8·6) is used in the electrode vessels.

H. F. W. KIRKPATRICK

3699. **Detection of haemoglobin, haemoglobin - haptoglobin complexes and other substances with peroxidase activity after zone electrophoresis.** J. A. Owen, H. J. Silberman and C. Got (Dept. of Biochem., Univ. of Melbourne, Carlton, Victoria, Australia). *Nature*, 1958, **182**, 1373.—Comparison of various reagents showed *o*-dianisidine to be the most satisfactory. This substance (100 mg) is dissolved in ethanol (70 ml); 1·5 *M* acetate buffer soln., pH 4·7 (10 ml) and H_2O (18 ml) are added. Immediately before use 100-vol. H_2O_2 (2 ml) is added to this soln. After electrophoresis, paper or starch-gel strips are placed in the reagent for 15 min. and are then washed in 3 changes of water and dried. Zones possessing peroxidase activity are stained brown - pink. H. F. W. KIRKPATRICK

3700. **Human haptoglobins: estimation and purification.** G. E. Connell and O. Smithies (Dept. of Biochem., Univ. of Toronto, Canada). *Biochem. J.*, 1959, **72** (1), 115–121.—A rapid and accurate method for the determination of haptoglobulin in serum or in purified preparations depends on the peroxidase activity of haemoglobin - haptoglobin complexes, H_2O_2 and guaiacol being used as the oxidising substrate and H donor, respectively. Reaction conditions are chosen so that the peroxidase activity of free haemoglobin is essentially zero. The formation of tetraguaiacol during the reaction is followed spectrophotometrically. The method is calibrated against a haemoglobin standard so that the haptoglobin content of a soln. can be expressed in terms of its haemoglobin binding capacity.

J. N. ASHLEY

3701. **Method for accurate determination of plasma albumin.** E. L. Kanabrocki, J. Greco, R. L. Veatch and L. Wilkoff (Veterans Admin. Hosp., Hines, Ill., U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (4), 661–666.—Errors arising from inconsistency in salting-out are minimised by the method described. Results for plasma albumin agree well with those obtained by electrophoresis. *Procedure*—To 0·25 ml of plasma in a test-tube (16 mm × 125 mm) add 7·75 ml of 26·8% Na_2SO_4 soln. at 37° and overlay with 3 ml of diethyl ether. Stopper the tube, invert 11 times in 30 sec. and then centrifuge at 900 *g* for 10 min. Tilt the tube to loosen the globulin layer and remove 2·0 ml of the underlying liquid for determination of N by the micro-Kjeldahl method.

W. H. C. SHAW

3702. **Improved periodic acid - fuchsine - sulphite staining method for evaluation of glycoproteins.** W. F. McGuckin and B. F. McKenzie (Sect. of Biochem., Mayo Clinic, Rochester, Minn., U.S.A.). *Clin. Chem.*, 1958, **4** (6), 476–483.—The method of Köiw and Grönwall (*Scand. J. Clin. Lab. Invest.*, 1952, **4**, 244) requires modification for application to the heavier type of filter-paper (Whatman 3MM). Preliminary washing of the dried strip with 95% ethanol is essential to remove buffer salts and ensure a suitable pH for oxidation, and the oxidation must be controlled at 20° ± 0·5° for 12 min. to ensure low background colour. Reduction with a metabisulphite - thiosulphate reagent is superior to the original method. The concn. of HCl in the dye bath and wash soln. is critical in affecting the quality of the staining. Preparation of the modified reagents and of the sample for analysis is described.

H. F. W. KIRKPATRICK

3703. **Method for assaying for glycoprotein in calcium fractionation.** B. Ravinowitch and R. Bartosiewicz (Argonne Cancer Res. Hosp., Univ., Chicago, Ill., U.S.A.). *Proc. Soc. Exp. Biol. Med.*, 1958, **99** (1), 42–43.—A method for the quant. or qual. determination of carbohydrate in samples involves the deposition of micro quantities of the samples on paper strips, staining with Köiw's stain and analysis of the results with the Spinco Analytol apparatus. The procedure has been described by Köiw and Grönwall (*J. Clin. Lab. Invest.*, 1952, **4**, 244).

B. P. BLOCK

3704. **Improvement in the protein-bound iodine method.** H. W. Marlow (Vet. Admin. Hosp., Downey, Ill., U.S.A.). *Clin. Chem.*, 1958, **4** (6), 510–512.—The addition of a specified amount of $KClO_3$ to the mixture in the incineration procedure eliminates unburned residue and shortens the time of heating.

H. F. W. KIRKPATRICK

3705. **Modification of the alkaline combustion method for the determination of protein-bound iodine in serum.** P. Vilkki (Surgical Clinic and Dept. of Pharmacol., Univ. of Turku, Finland). *Scand. J. Clin. Lab. Invest.*, 1958, **10** (3), 272–277.—In the method of Barker *et al.* (*J. Clin. Invest.*, 1951, **30**, 55), pptn. of proteins is replaced by dialysis in Cellophane bags against tap water. The water used must not contain >10 μg of iodine per litre, and dialysis must continue for ≮12 hr. The dialysis bags and contents are ashed with an alkali - catalyst reagent (70·1 g of KOH and 25·0 g of $ZnSO_4$, each dissolved in 250 ml of H_2O and mixed immediately before use), in nickel crucibles at 600°, followed by extraction of the ash with strong alkali. The recovery of added iodide, which is checked with each series of analyses, shows that the dialysis procedure extracts all inorganic iodide. The modified procedure gave a mean value for protein-bound iodine in 20 sera which was 0·26 μg per 100 ml higher than that obtained by pptn., but this is not significant. The method is suitable for the determination of iodine in other tissues and in foodstuffs.

D. W. MOSS

3706. **Spectrophotometry in the far-ultra-violet region. II. Absorption spectra of steroids and triterpenoids.** D. W. Turner (Imperial Coll., London). *J. Chem. Soc.*, 1959, 30–33.—The spectra of some 36 steroids and triterpenoids and other simpler compounds are corrected for the high-intensity absorption at 176 mμ (related to the number of quaternary C centres) by subtraction of the spectrum of the dihydro compound. The $\lambda_{max.}$ of the corrected curves resemble those of simpler olefins and are correlated with the degree of double-bond substitution (4 substituents, 200 to 196; 3, 193 to 188; 2, 188 to 182 mμ). As exceptions, geminally di-substituted olefins absorb at abnormally long wavelengths (attributable to a dipole-moment vector effect), and a bathochromic shift is observed in certain members of the tri-substituted group, particularly in Δ^7-compounds. The attribution of the second type of exception to steric strain is discussed.

E. J. H. BIRCH

3707. **Mass spectra of steroids.** S. S. Friedland, G. H. Lane, jun., R. T. Longman, K. E. Train and M. J. O'Neal, jun. (Dept. of Physics, Univ. of Connecticut, Storrs, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 169–174.—Pyrolysis of the sample at 350° for 30 min. followed by mass spectrometry gives results sufficiently reproducible for the identification of a single steroid and for the quant. analysis of simple mixtures. By the use of a heated (200°) gas-inlet system in a mass spectrometer, characteristic cracking patterns are obtained which give much information about the molecular structure as well as the molecular weight of the sample. About 1 mg of sample is adequate.

A. R. ROGERS

3708. **Isolation, characterisation and measurement of steroid glucuronides in human plasma.** G. L. Cohn and P. K. Bondy (Dept. of Internal Med., Yale Univ. Sch. of Med., New Haven, Conn., U.S.A.). *J. Biol. Chem.*, 1959, **234** (1), 31–34.—A method is described for the determination of the glucuronides of tetrahydrocortisone and tetrahydrocortisol in plasma. The conjugated steroids are separated from the non-conjugated steroids by paper electrophoresis and paper chromatography. Each glucuronide is then determined by the carbazole reaction. An isotope dilution method is

also described; it is used with [4-^{14}C]tetrahydrocortisone glucuronide to correct the results to 100% recovery. J. N. ASHLEY

3709. **Isolation of oxosteroids under neutral conditions.** W. Taylor (Physiol. Dept., Med. Sch., King's College, Newcastle upon Tyne). *Nature*, 1958, **182**, 1735.—The method of Teitelbaum (*J. Org. Chem.*, 1958, **23**, 646) for the isolation of labile ketones has been applied to the ketosteroids progesterone (**I**) and pregnanediolone (**II**). Dissolve the steroid (10 mg) in ethanol (1 ml) and add Girard reagent T (20 mg) and Amberlite IRC-50 cation-exchange resin (5 mg). Heat under reflux for 1 hr. or allow to stand at room temp. for 24 hr. Add H_2O (10 ml) and extract non-ketonic material with solvent (diethyl ether for **I** or ethyl acetate for **II**). Add 40% formaldehyde soln. (2 ml), allow to stand overnight and extract the ketosteroid with solvent. The recovery is >90%, with <1% appearing in the non-ketonic fraction. A. R. ROGERS

3710. **Spectrophotometric determination of Δ^{4}-3-oxosteroids with salicylhydrazide. Application to urinary aldosterone.** P. S. Chen, jun. (Sect. of Clin. Endocrinol., Nat. Heart Inst., Nat. Inst. of Health, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 292–296.—Salicylhydrazide reacts with cortisone, cortisol, aldosterone, corticosterone, testosterone and progesterone to form characteristic hydrazones which absorb strongly at 295 mμ. Their analytical use is exemplified by the determination of aldosterone in urine. *Procedure*—Extract the urine at pH 1 with dichloromethane for 20 hr. Purify the extract by paper chromatography, first with the C system of Bush (*Biochem. J.*, 1952, **50**, 370), and then with the E_2B system of Eberlein and Bongiovanni (*cf. Anal. Abstr.*, 1956, **3**, 3160). Elute the aldosterone zone with ethanol, evaporate to dryness and allow to react with salicylhydrazide in ethanolic acetic acid at 60° for 30 min. Remove excess of reagents and other impurities by paper-chromatographic development with benzene satd. with H_2O; aldosterone salicylhydrazone remains at the origin. Extract with 50% ethanol and measure the extinction at 295 mμ; correct for the filter-paper blank by the method of Allen (*J. Clin. Endocrinol.*, 1950, **10**, 71). A loss of about 15% of the steroid occurs at each chromatographic separation step, and a correction should be applied. The results of 6 replicate determinations of aldosterone in a 6-hr. urine sample ranged from 15·8 to 20·1 μg. A. R. ROGERS

3711. **Production of fungal amylase. I. Fuwa's method of determination of β-amylase.** Nobuhiko Yamada (Inst. for Fermentation, Juso-Nishino-cho, Higashi-yodogawa-ku, Osaka). *J. Agric. Chem. Soc. Japan*, 1958, **32** (8), 581–583.—Fuwa's method for the determination of β-amylase (**I**) with amylose in 0·5 *M* acetate buffer (*J. Biochem. Japan*, 1954, **41**, 583) was kinetically examined with reference to its application to the determination of low concn. of **I**. By decreasing the final vol., the limit of determination was decreased to one tenth. The hydrolysis apparently proceeds as a first-order reaction; the amount of the reagents must not be decreased. The sample soln. (10 ml) is mixed with 0·5 *M* acetate buffer (pH 5·4) and 0·2% amylose soln., and kept at 37° for 30 min.; the resulting sugar is determined by Nelson's molybdoarsenate method (vol. 10 ml). K. SAITO

3712. **Carbonic anhydrase. A spectrophotometric assay.** P. K. Datta and T. H. Shepard (Washington Univ., Seattle, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **79**, 136–145.—In the method described, 1·0 ml of aq. phenol red soln. (pH 6·0), containing 12·5 μg of indicator, and 1·5 ml of water are placed in the reference cell of a recording spectrophotometer set at 560 mμ. In the sample cell are placed 1·0 ml of the same phenol red soln. and 1·5 ml of test soln. or water. Both soln. are equilibrated for 2 min. in the cell compartment maintained at 4° to 5° with cooled 95% ethanol, while CO_2 (12 ml per min.) is passed through the cells. After recording the base line, 1·0 ml of 0·0286 *M* tri(hydroxymethyl)-methylamine buffer (pH 9) is injected into the sample cell, and the time taken for the extinction difference to fall to 0·20 is measured. The difference in time required for this to occur for water and for the test soln. is a measure of enzyme activity. W. H. C. SHAW

3713. **Rapid colorimetric method for the quantitative determination of copper oxidase activity (ceruloplasmin).** O. B. Houchin (Dept. of Neurol., Univ. of Arkansas Sch. of Med., Little Rock, U.S.A.). *Clin. Chem.*, 1958, **4** (6), 519–523.—*Procedure*—To 1·0 ml of freshly prepared 0·1% *p*-phenylenediamine in acetate buffer (pH 5·2) at 37°, serum (0·1 ml) is added. After incubation for 15 min. at 37°, 0·02% sodium azide soln. (5·0 ml) is added to stop the reaction, and the extinction is read against a blank (water or reagent) at 525 mμ. Correlation of the extinction with ceruloplasmin concn. determined by the method of Scheinberg *et al.* (*Science*, 1957, **126**, 925) is employed for calibration and shows a straight-line relationship. H. F. W. KIRKPATRICK

3714. **Colorimetric micro-method for the determination of cholinesterase.** D. E. McOsker and L. S. Daniel (Cornell Univ., Ithaca, N.Y., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **79**, 1–7.—A rapid sensitive method is described for the determination of cholinesterase activity, with acetylthiocholine as substrate. The method is applied to the assay of animal brain, blood and plasma. *Procedure*—Place, in a 15-ml centrifuge tube, 0·20 ml of 0·015 *M* acetylthiocholine iodide, 0·50 ml of 0·125 *M* tri-(hydroxymethyl)methylamine buffer (pH 7·4), 0·20 ml of 3·5 *M* NaCl and water to 1·30 ml. Warm to 37°, add 0·10 ml of tissue homogenate and incubate for 10 min. Add 0·10 ml of 25% w/v trichloroacetic acid (or of 50% w/v soln., if necessary to produce a clear supernatant liquid) and centrifuge. Place in a spectrophotometer cell 2·0 ml of satd. aq. NaCl soln., 0·4 ml of Na_2CO_3 - NaCN soln. (21·2 g of Na_2CO_3 and 0·44 g of NaCN in water to 100 ml) and 0·4 ml of sodium nitroprusside soln. (27 mg per ml). Mix, add 0·2 ml of the supernatant liquid and after exactly 30 sec. measure the extinction at 520 mμ. W. H. C. SHAW

3715. **Investigations on the enzymes of human blood. I. Photometric micro-determination of acetylcholinesterase in serum and erythrocytes.** W. Pilz (Ärzlich. Abt., Farbenfabrik. A.-G., Bayer, Leverkusen, Germany). *Klin. Wochschr.*, 1958, **36** (21), 1017–1021.—The rapid method described requires 0·02 ml of blood, and is based on measurement at 490 mμ of the red colour formed when Fe^{3+} react with acetohydroxamic acid produced by the action of unchanged acetylcholine on hydroxyl-

amine in alkaline soln. The various factors affecting the determination were investigated, including the specificity of the enzyme for different substrates. D. B. PALMER

3716. **Glutamic - aspartic transaminase. I. Assay, purification and general properties.** W. T. Jenkins, D. A. Yphantis and I. W. Sizer (Div. of Biochem., Dept. of Biol., M.I.T., Cambridge, Mass., U.S.A.). *J. Biol. Chem.*, 1959, **234** (1), 51–57.—A spectrophotometric method is described for the assay of the transaminase. It is based on the determination, at 280 mμ, of the enol form of oxaloacetate which is in equilibrium with the oxo form produced in the reaction between aspartate and α-oxoglutarate in the presence of the enzyme. J. N. ASHLEY

3717. **Stable test-papers for seminal acid phosphatase.** S. S. Kind (Home Office Forensic Sci. Lab., Rutland Drive, Harrogate, Yorks., England). *Nature*, 1958, **182**, 1372–1373.—Dissolve 1-naphthyl phosphoric acid (200 mg) and diazo-*o*-dianisidine (Brentamine Fast Blue B Salt) (C.I. Azoic Diazo Component 48) (400 mg) in 0·2 *M* citric acid - Na citrate buffer soln., pH 4·9 (100 ml); soak a filter-paper in this soln. and allow to dry at room temp. in subdued light. Store in a light-proof bottle. Apply a wet filter-paper to the stain and place a moistened test-paper on this; a positive reaction is shown by an intense purple colour formed on the intermediate paper. The test-paper remains usable for a year. H. F. W. KIRKPATRICK

3718. **Studies on sulphatases. XXIV. Use of barium chloranilate in the determination of enzymically liberated sulphate.** A. G. Lloyd (Dept. of Biochem., Univ. of Wales, Newport Rd., Cardiff). *Biochem. J.*, 1959, **72** (1), 133–136.—A modification of the Ba chloranilate method (*cf.* Bertolacini and Barney, *Anal. Abstr.*, 1957, **4**, 2580) is described for the determination of small amounts (5 to 80 μg per 0·2 ml) of sulphate. After the pptn. of $BaSO_4$, the amount of chloranilate ion released into the soln. is determined at 350 mμ. There is a linear relation between the concn. of sulphate and the spectrophotometric reading. The presence of other anions does not affect the result, but NH_4^+, Ca^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}, Pb^{2+} and Cu^{2+} interfere. The method, which effects a considerable saving in time, compares favourably with the benzidine method. Within certain limits the assay is unaffected by the presence of the assay substrates for carbohydrate sulphatases. J. N. ASHLEY

3719. **The electrophoresis and titration of fumarase. [Determination of fumarase.]** N. Shavit, R. G. Wolfe and R. A. Alberty (Dept. of Chem., Univ., Wisconsin, Madison, U.S.A.). *J. Biol. Chem.*, 1958, **233** (6), 1382–1386.—The concn. of active enzyme in a soln. is determined by adding L-malate and determining the steady-state rate of dehydration to fumaric acid from the rate of change of absorbance in the u.v. region. The enzyme soln. is diluted with 0·05 *M* phosphate buffer (pH 7·3). To the dil. soln. (3 ml) add 0·35 *M* K L-malate (0·5 ml) which also contains 0·05 *M* phosphate buffer. Measure the change in absorbance per 10 sec. at 250 mμ, with a 1-cm cell. The change in absorbance divided by 31·5 gives the amount of fumarase in mg in 3 ml of the dil. soln. J. N. ASHLEY

3720. **The presence of pyruvate as a source of error in ammonia determinations by means of Nessler's reagent.** G. Steensholt and L. Rotnes (Dept. of Biochem., Oslo Univ., Norway). *Acta Chem. Scand.*, 1959, **13** (1), 189–190 (in English).—The colours of Nessler reagent with added NH_4^+ were reduced in the presence of pyruvate (15·9 μmoles per 9 ml of final soln.) by about 50% for Vanselow's, and 24% for Kolthoff's, Nessler reagent, both used with Archibald's persulphate - gluconate stabiliser. For the determination of pyruvate-activated glucaminase II, a calibration curve prepared by adding pyruvate to the NH_4^+ standards should be used. To allow for loss of pyruvate during incubation, 80% of the initial amount of pyruvate should be added to the blank, after adding H_2SO_4 on termination of the incubation (Beaton, *Proc. Soc. Exp. Biol. Med.*, 1954, **87**, 238). D. G. Moss

---

See also Abstracts—**3457**, Determination of NH_3 in biological fluids. **3495**, Chlorine in distilled water as a source of error. **3503**, Determination of iodine in serum. **3584**, Determination of cysteine. **3601**, Catecholamines in urine. **3648**, Determination of Ca in serum. **3745**, Determination of thiohydantoins in urine. **3763**, Determination of lysine in milk. **3769**, Phenolic constituents in *Prunus domestica*. **3780**, Unsaturated fatty acids in plasma. **3785**, Microbiological assay of amino acids. **3813**, Sedimentation analysis. **3818**, Fraction collector for amino acids. **3820**, Chromatography of amino acids. **3823**, Chromatography of quaternary ammonium compounds. **3852**, Sodium in biological systems. **3854**, Source of error in radioactive counting.

Pharmaceutical analysis

3721. **Modern analytical chemistry in the service of pharmacy and medicine.** G. E. Foster (Wellcome Chem. Works, Dartford, Kent, England). *J. Pharm. Pharmacol.*, 1958, **10**, Supplement, 9T–23T.—A review with 59 references. A. R. ROGERS

3722. **Colorimetric determination of morphine in galenical preparations.** C. A. Johnson and C. J. Lloyd (Standards Dept., Boots Pure Drug Co. Ltd., Nottingham, England). *J. Pharm. Pharmacol.*, 1958, **10**, Supplement, 60T–71T.—Improved extraction procedures are suggested for the separation of morphine from extraneous material in camphorated tincture of opium, opiate linctus of squill, compound camphorated linctus of opium, ammoniated tincture of opium, opiate pastilles of squill and tincture of chloroform and morphine (*cf.* Garratt *et al.*, *Anal. Abstr.*, 1958, **5**, 2754). The application of the colorimetric method of Pride and Stern (*cf. Anal. Abstr.*, 1954, **1**, 3093) to the morphine residues so obtained is described. A. R. ROGERS

3723. **Comparative study of the hydrolytic and non-hydrolytic methods for the assay of solanaceous drugs.** R. E. A. Drey (Wellcome Chem. Works, Dartford, Kent, England). *J. Pharm. Pharmacol.* 1958, **10**, Supplement, 241T–246T.—The results obtained by the hydrolytic and non-hydrolytic methods for the determination of the total alkaloid content are in good agreement for belladonna, stramonium and hyoscyamus. The agreement is fair for *Duboisia leichhardtii* and *Datura sanguinea*, whilst for *Duboisia myoporoides* the non-hydrolytic

method gives spuriously high results. The hydrolytic method is recommended for the assay of duboisia samples and for Indian belladonna. Oscine, tropine, belladonnine, hyoscine, valeroidine, tigloidine and apoatropine can be separated from each other and from hyoscyamine and norhyoscyamine by descending chromatography, on Whatman No. 1 paper treated with 0·2 *M* KCl, with a H_2O-saturated mixture of *n*-butanol - *n*-butyl acetate - glacial acetic acid (3:17:8) as solvent.

A. R. ROGERS

3724. **Interference of autoxidised ether in analysis of alkaloids and other organic bases. III. Determination of alkaloids of belladonna extract.** B. Samdahl and E. H. Vihovde (Pharm. Chem. Lab., Univ., Oslo, Norway). *Medd. Norsk Farm. Selsk.*, 1959, **21** (1), 1–8.—When treated with diethyl ether containing 0·1% of peroxides (as H_2O_2) under the conditions obtaining in the Norwegian official method for the determination of alkaloids in the extract, hyoscyamine is shown by paper-chromatographic analysis to be completely oxidised to genohyoscyamine. The effect of ether containing 0·025% of peroxides is negligible. Similar results are obtained for atropine. As the genoalkaloids are not titratable with HCl to methyl red, the titration results obtained after the use of autoxidised ether will be low. These results are analogous to those found for the nux vomica alkaloids (*cf. Anal. Abstr.*, 1959, **6**, 2745). P. S. ARUP

3725. **Quantitative determination of the sum of alkaloids belonging to various groups in ergot.** H. Speichert (Inst. of Medicinal Plants, Poznan). *Acta Polon. Pharm.*, 1959, **16** (1), 51–56.—A new method for the quant. determination of the alkaloids belonging to three groups (ergometrine, ergotamine and ergotoxine) has been developed. An aliquot of the pulverised and de-fatted ergot is extracted with diethyl ether and the ether extract is placed on a non-impregnated Whatman No. 3 paper. The mobile phase comprises benzene - toluene - light petroleum - methanol (12:5:5:2). Development of the chromatogram takes ≃3 hr. Quant. results are obtained by eluting the cut-out spots of the alkaloid groups with a 0·5% soln. of tartaric acid in methanol and developing the colour with Allport's reagent; semi-quant. results are obtained by comparing a chromatogram of pure alkaloid standards with that of the tested extract in u.v. light. W. B. MIASKOWSKI

3726. **Micro-identification of rauwolfia alkaloids by paper electrophoresis and multi-buffered paper chromatography.** Hidehiko Kaneko (Res. Lab., Dainihon Pharm. Co., Kami-ebie, Fukushima-ku, Osaka). *J. Pharm. Soc. Japan*, 1958, **78** (5), 512–515.—Nine alkaloids in Indian snakewood (*Rauwolfia serpentina* Benth.) were separated by paper electrophoresis (500 V, 2 to 4 hr.) with 0·1 *N* citric acid or *N* acetic acid as electrolyte. Each spot was detected by fluorescence or with Dragendorff reagent. The rate of migration increased in the order rescinnamine, reserpine, reserpinine, serpentine, sarpagine, ajmalicine, yohimbine, ajmaline and serpentinine. By multi-buffered paper chromatography with $CHCl_3$ - benzene (1:2), *i.e.*, by the use of a paper impregnated at regular intervals with citrate buffers of pH 6·4, 5·8, 5·5, 5·2, 4·9, 4·6, 4·3, 4·0, 3·0 and 2·1, the spots of these alkaloids were found at pH 4·3, 4·6, 3·0, 7·0, 7·0, 4·0, 5·5, 6·1 and 6·4, respectively (at pH 7·0 the spots remain at the origin). K. SAITO

3727. **Decomposition products of reserpine and their influence on the determination of reserpine.** K. G. Krebs and N. Futscher (Univ.-Apotheke, Tübingen, Germany). *Dtsch. ApothZtg*, 1958, **98** (52), 1341–1344.—Deteriorated preparations of reserpine (**I**) give results by the column-chromatographic method of Bartelt and Hamlow (*cf. Anal. Abstr.*, 1956, **3**, 1478) and the fluorimetric method of McMullen *et al.* (*Ibid.*, 1956, **3**, 509) which accord with the stated content of **I**, whilst the colorimetric vanillin - HCl method of Banes (*Ibid.*, 1956, **3**, 510) gives much lower results. It is found that the primary product of the decomposition of **I** (possibly 3:4-dehydroreserpine), which appears in chromatograms as a green spot under u.v. light, gives no coloration with vanillin and HCl. A spectrophotometric method is described for the determination of **I** which depends on the quant. conversion of **I** into the primary decomposition product by treatment under standard conditions with $NaNO_2$ and acetic acid; the product is distinguished by a specific absorption maximum at 388 mμ. Comparisons are made with similarly treated soln. of pure **I**. The content of the decomposition product originally present in deteriorated samples is determined by spectrophotometric measurement of untreated soln. of the samples, and deducted from the total. The reproducibility of the method is satisfactory. Results are accurate to within ±1·2% for tablets, and ±0·7% for soln. Drugs commonly used in combination with **I**, or substances used in preparing tablets, do not interfere. P. S. ARUP

3728. **Detection reactions for 1-(dihydroxypropyl)-theobromine and 7-(dihydroxypropyl)theophylline and a critical comparison with those for caffeine, theobromine and theophylline.** R. Ott and (in part) H. Wittmann-Zinke (Inst. für Organ. und Pharm. Chem., Univ., Graz). *Sci. Pharm.*, 1958, **26** (4), 217–224.—A review is presented, with 26 references, of pptn. and colour tests and paper-chromatographic methods of detection of caffeine, theobromine and theophylline. The behaviour of 1-(dihydroxypropyl)theobromine and 7-(dihydroxypropyl)theophylline in these tests is described.

A. R. ROGERS

3729. **Determination of alkaloids in aluminium oxide columns. II. Caffeine in caffeine citrate, caffeine sodium salicylate, caffeine sodium benzoate, caffeine benzoate, "Coffea" tincture HAB, filtered coffee and Nescafé powder.** K. Pfandl (Wissenschaftl. Abteil. der Firma Chem.-pharm. Fabrik, Müller/Göppingen). *Dtsch. ApothZtg*, 1959, **99**, 141–143.—Caffeine may be determined in these preparations by passing them, in a water - ethanol medium, through a chromatographic column of basic aluminium oxide. A mixture of $CHCl_3$ and diethyl ether, used as eluent, dissolves the caffeine, which is then weighed after evaporation of the solvent. M. H. SAWISTOWSKA

3730. **Digitalis glycosides. II. Influence of method of drug extraction on results of paper-chromatographic analysis of digitalis leaves (*Digitalis lanata* Ehrh. and *D. purpurea* L.).** L. Fuchs, M. Wichtl and H. Jachs (Pharmakog. Inst. Univ., Wien). *Arch. Pharm., Berlin*, 1959, **292** (1), 15–20.—Procedures for hot and cold extraction of digitalis leaves with water and 20% and 70% ethanol are described. Paper-chromatographic analysis shows the highest content of glycosides in the hot 70% ethanol extract. With cold-water extraction, substantial fermentative degradation of primary glycosides takes place. M. H. SAWISTOWSKA

3731. **Chemical evaluation of digitalis drugs (*Digitalis purpurea* and *D. lanata*). Preliminary report.** W. Hauser and I. Mathauser (Pharmakog. Inst. Univ., Graz). *Sci. Pharm.*, 1958, **26** (4), 258–262.—The use of Pb acetate in the purification of aq. extracts of digitalis before assay may lead to losses of glycosides of up to 14%; with basic Pb acetate, losses may be up to 30%. In the method described, interference caused by flavones is eliminated by use of CaO. *Procedure*—Dilute the filtered hot-water extract (50 ml ≡ 0·5 g of drug) with water (30 ml) and boil gently for 15 min. with dil. HCl (12·5%) (5 ml). Cool, neutralise with dil. aq. NH_3 (10%) and extract with diethyl ether (4 × 20 ml). Treat the combined extracts with powdered CaO (2 g) and with anhyd. Na_2SO_4 (3 g) and filter. Wash the residue with ether (2 × 15 ml). Evaporate the filtrate and washings to dryness under reduced pressure, dissolve the residue in ethanol (10 ml) and assay by the 3:5-dinitrobenzoic acid method. A. R. ROGERS

3732. **Separation and determination of the primary and secondary glycosides of *Digitalis purpurea* leaf.** J. Lemli (Lab. de Pharmacog., Inst. de Pharm., Louvain, Belgium). *Pharm. Acta Helv.*, 1959, **34** (1), 19–28 (in French).—Prepare a 1:10 tincture with 70% ethanol and transfer to a chromatographic column of Al_2O_3 (Brockmann grade III). Elute chlorophyll and other coloured matter with diethyl ether and discard. Elute digitoxin, odoroside H, gitoxin, gitaloxin, strospeside, verodoxin and derivatives of diginin with $CHCl_3$ - methanol (9:1). Pass more ether through the column, and then elute purpurea glycosides A and B, glucogitaloxin, digitalinum verum and gitorin with 35% aq. ethanol. The glycosides are determined colorimetrically in alkaline ethanolic soln. at 540 mμ by the 3:5-dinitrobenzoic acid reaction after hydrolysis with 0·4 *N* HCl to the aglycones. Some species of digitalis contain colouring matter which is insol. in ether but sol. in $CHCl_3$ - methanol (9:1) and causes interference; this is corrected by using as a blank an alkaline soln. of the eluate which has not been treated with 3:5-dinitrobenzoic acid.
A. R. ROGERS

3733. **Reaction between dinitro derivatives and active methylene compounds. I. Colorimetric determination of cardiotonic glycosides with 3:5-dinitrobenzenesulphonic acid.** Masami Akatsuka (Pharm. Fac., Kumamoto Univ., Kihonji). *J. Pharm. Soc. Japan*, 1958, **78** (1), 62–64.—Potassium 3:5-dinitrobenzenesulphonate (**I**) gives a red colour (max. absorption at 530 mμ) with active methylene compounds such as digitoxin (**II**), strophanthin (**III**) and ouabain (**IV**) in alkaline soln. The extinction is proportional to the concn. of **II**, **III** and **IV** for <10 mg per 100 ml. With increase in concn. of alkali, the colour develops and fades faster. The sample is extracted with methanol and diluted, and a 4-ml aliquot is mixed with **I** soln. (5%) (0·5 ml) and KOH soln. (5%) (0·5 ml); the extinction is measured at 530 mμ after 10 min.
K. SAITO

3734. **Application of a spectrophotometric method to the determination of potassium penicillin, procaine penicillin and benzathine penicillin in pharmaceutical preparations.** A. Holbrook (I.C.I., Ltd., Pharmaceuticals Div., Blackley, Manchester). *J. Pharm. Pharmacol.*, 1958, **10** (12), 762–769.—Penicillin is determined spectrophotometrically after degradation to penicillinic acid by heating with acetate buffer (pH 4·6) in the presence of a trace of Cu^{2+}. The method has a standard error of 3%. It is applicable to a variety of ointments, lozenges, injections and other preparations of penicillin after preparation of an appropriate extract. The results are in good agreement with those obtained microbiologically. A. R. ROGERS

3735. **Colorimetric estimation of phenoxymethylpenicillin (penicillin V) and phenoxyacetic acid in samples from penicillin fermentations.** J. Birner (Commonwealth Serum Lab., Melbourne, Australia). *Anal. Chem.*, 1959, **31** (2), 271–273.—The method depends on the yellow colour given in ammoniacal soln. by the derivatives formed by the nitration of phenoxymethylpenicilloic acid (**I**) [the product of alkaline hydrolysis of penicillin V (**II**)] and of phenoxyacetic acid (**III**); **III**, but not **I**, is extracted by benzene from a satd. aq. soln. of $(NH_4)_2SO_4$ at pH 2; both **I** and **III** are extracted by *iso*butyl methyl ketone from a similar soln. As little as 12 μg of **II** and 5 μg of **III** can be determined.
A. R. ROGERS

3736. **Chromatograpic assay method for determining insulin in whale pancreas extract.** Yuichi Sasano and Katsumi Higashi (Res. Lab., Taiyo Fisheries Co., Tsukishima, Chuo-ku, Tokyo). *J. Pharm. Soc. Japan*, 1958, **78** (4), 424–427.—For the paper-chromatographic separation of insulin (**I**) (R_F 0·21 to 0·26) with a mixture of acetic acid, butanol and water (1:6:7, by vol.) (*cf. Anal. Abstr.*, 1957, **4**, 3426), the total protein must be <3 mg and the total electrolyte <5 mg (as NH_4Cl). The electrolytes are removed by dialysis and **I** is concentrated by evaporation at 30° to 34°. The spot is stained with 0·02% bromocresol green and the combined indicator is extracted from the cut-out spot with borate - NaOH buffer, and the extinction is measured at 620 mμ. K. SAITO

3737. **Quantitative determination of nicotinic acid in some pharmaceutical preparations with the aid of cation exchanger Wofatit KPS-200.** K. Howorka (Staatl. Inst. für Arzneimittelprüf., Jena). *Pharm. Zentralh.*, 1958, **97** (11), 521–524.—To determine sodium nicotinate, apply an aq. soln. of the sample (50 to 250 mg) to a column of Wofatit KPS-200 in the pyridine form, elute with H_2O (250 ml), and titrate the eluate with 0·1 *N* KOH. Perform a blank titration to compensate for CO_2 in the water. Compensate for the presence of mineral salts by titration of the eluate resulting from the passage of a duplicate sample through a column of the H^+ form of the resin. Esters and amides of nicotinic acid and preparations may be assayed by application of the method to the products of saponification. A. R. ROGERS

3738. **Assay of nicotinamide in tablets and injections by non-aqueous titration.** H. H. Kavarana (Anal. and Standardisation Dept., Worli Chem. Works, Bombay, India). *Indian J. Pharm.*, 1958, **20** (12), 360–361.—Nicotinamide in B-complex tablets and injections is separated from interfering substances by its solubility in acetone, and is titrated with $HClO_4$ in glacial acetic acid. *Procedure*—A sample of B-complex tablet containing ≃100 mg of nicotinamide is extracted with acetone (6 × 20 ml) and the filtrate is evaporated to dryness. The dry residue is dissolved in 20 ml of glacial acetic acid and 12 drops of methyl violet (0·2% w/v in chlorobenzene) are added. On titrating with 0·1 *N* $HClO_4$ in glacial acetic acid the wine-red colour turns green on the approach of the end-point,

and the end-point is reached when a yellow colour persists for 1 min. The acid is standardised with 100 mg of pure nicotinamide, and a permanent blue colour indicates the end-point. Injections are evaporated to dryness and the residue treated in the same way as the tablets. Riboflavine does not interfere except in large excess (unlikely in practice). Excipients (not containing glucose or sucrose), disintegrating agents and even chocolate coating do not interfere. Preparations in a syrup or malt base cannot be determined in this way owing to incomplete extraction of the sticky residue by acetone. E. J. H. BIRCH

3739. **Studies on streptomycetes. Assay of vitamin B_{12} in the presence of dihydrostreptomycin.** Koiti Nakazawa, Motoo Shibata, Hiroichi Yamamoto, Eiji Higashide and Toshihiko Kanzaki (Inst. for Fermentation, Juso-nishinocho, Higashiyodogawa-ku, Osaka). *J. Agric. Chem. Soc. Japan*, 1958, **32** (5), 399–405.—The effect of dihydrostreptomycin (**I**) on the bioassay of B_{12} in a fermenting culture of *Streptomyces humidus*, with an *Escherichia coli* mutant (No. 313) or *Lactobacillus leichmannii* was examined. The presence of <1 μg or $<0{\cdot}2$ μg of **I** per ml of the culture does not cause interference when *Esch. coli* or *Lb. leichmannii*, respectively, is used. No interference results from <2 μg of other antibiotics, including oxytetracycline, chloramphenicol, chlortetracycline and penicillin. By successive cultivation (12 generations), a strain resistant to 1 mg of **I** per ml was obtained, its response towards B_{12} remaining unchanged. The resistant strain is applicable to the determination of B_{12} by the use of a medium containing (per litre) K_2HPO_4 (14 g), KH_2PO_4 (6 g), $(NH_4)_2SO_4$ (2 g), $MgSO_4.7H_2O$ (0·2 g), citric acid (0·8 g), NaCl (5 g), L-asparagine (4 g), DL-tryptophan, L-glutamic acid, L-arginine hydrochloride, L-histidine hydrochloride, glycine, proline (0·4 g each) and glucose (4 g). K. SAITO

3740. **Pharmacognostic studies of drugs containing coumarin and its derivatives. III. Chromatographic separation and colorimetric determination of umbelliferone and its homologues.** Mitiiti Fujita, Tsutomu Furuya and Hideji Itokawa (Fac. Pharm., Tokyo Univ., Hongo). *J. Pharm. Soc. Japan*, 1958, **78** (4), 395–398.—The red colour (max. absorption, 510 mμ) produced by the action of 4-aminophenazone (**I**) and $K_3Fe(CN)_6$ on umbelliferone (**II**) in Na_2CO_3 soln. obeys Beer's law for <400 μg of **II** per ml. The hydrolysis of **II** is complete within 20 min. in 0·5% Na_2CO_3 soln. The separation of **II** from asafoetida, galbanum and ammoniacum (ethanolic extract) is effected by paper chromatography on paper treated with 0·1 *M* borate, and with butanol satd. with water as developing agent. An unidentified sulphur-containing substance in asafoetida gives a spot of the same R_F value, and two-dimensional chromatography is used with $CHCl_3$ and butanol as developing agents. The spot is cut out, boiled with 0·5% Na_2CO_3 soln. (10 ml) for 20 min., cooled for 30 min., mixed with **I** soln. (0·9% aq.) (0·4 ml) and $K_3Fe(CN)_6$ soln. (5·4%) (0·2 ml), and the extinction is measured after 1 hr. K. SAITO

3741. **Determination of crude fat in crude drugs by capillary analysis.** Yoshiaki Okazaki (Public Health Lab., Marunouchi, Kōchi). *J. Pharm. Soc. Japan*, 1958, **78** (6), 684–686.—The use of capillary analysis of the xylene extract of torreyanu, armenica, peanut, datura seed, pharbitis, etc., has been studied. The concn. of fat (x) in the xylene is related to the capillary elevation (y) by the empirical equation $y = 2^{m-nx}$, where m and n are constants for a given drug. Values of m and n are given for the drugs named. The results agree well with those by the usual Soxhlet extraction method. K. SAITO

3742. **Systematic identification of organic poisons by paper chromatography. I. Detection and separation of hypnotics.** Hisao Tsukamoto and Minoru Yoshimura (Pharm. Inst., Med. Fac., Kyushu Univ., Katakasu, Fukuoka). *J. Pharm. Soc. Japan*, 1958, **78** (1), 23–27.—The R_F values of derivatives of barbituric acid (**I**) (Kaiss and Lang, *Öst. ApothZtg*, 1955, **9**, 558), thiobarbituric acid (**II**) (Heise and Kimbel, *Arzneimittel-Forsch.*, 1955, **5**, 149) and diphenylhydantoin (**III**) (Curry, *Analyst*, 1956, **80**, 901), determined by the use of a mixture of aq. NH_3 soln. and organic solvents such as $CHCl_3$, propanol and butanol, decrease with increase in concn. of NH_3. It appears that the R_F value decreases with the ease with which enolisation takes place. For the separation of **I** derivatives, a mixture of butanol, $CHCl_3$ and 28% aq. NH_3 soln. (3:3:4) is preferred; for the separation of **I** and **II** derivatives, a mixture of *iso*propyl alcohol, acetone and 28% aq. NH_3 soln. (5:5:1) is used. By the use of butanol satd. with 10% aq. NH_3 soln., the spots of barbiturate, thiobarbiturate, **III** and bromoacylureas (**IV**) can be separated.

II. Colour reagents for the spot test of hypnotics on filter-paper. Hisao Tsukamoto and Minoru Yoshimura. *Ibid.*, 1958, **78** (1), 27–29.—Whilst the Cu - pyridine complex (Zwikker, *Pharm. Weekbl.*, 1931, **68**, 975) gives a pink colour with compounds containing the structural units $=N{\cdot}CO{\cdot}N=$, $=N{\cdot}CS{\cdot}N=$ and $=N{\cdot}C{:}N-$, the use of aq. $AgNO_3$ soln. (0·05%) (Sabatino, *cf. Anal. Abstr.*, 1955, **2**, 1013) permits the separation of **I**, **II** and **IV**. Cobaltammine soln. (*cf.* Posez, *J. Pharm. Chim.*, 1938, **28**, 69) gives a positive reaction with those compounds that have an imino group which is capable of dissociating to give H^+. K. SAITO

3743. **Applications of nitrometry. XV. Determination of phenazone.** Masaharu Yamagishi, Makoto Yokoo and Saburo Inoue (Res. Lab., Takeda Pharm. Ind., Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1958, **78** (1), 87–90.—Phenazone is converted within 2 min. to 2-nitrosophenazone (**I**) by the use of KNO_2 in dil. H_2SO_4, and the excess of NO_2^- is determined, by a nitrometer, with sulphamic acid (**II**). Alternatively, **I** is readily reduced to 2-aminophenazone with zinc dust and the product is determined, by a nitrometer, with **II** and NaN_3. K. SAITO

3744. **Note on the analysis of diphenylhydantoin sodium by an ion-exchange procedure.** M. C. Vincent and M. I. Blake (N. Dakota Agric. Coll., Sch. of Pharm., Fargo, U.S.A.). *Drug Standards*, 1958, **26** (6), 206–207.—Dissolve the pure diphenylhydantoin sodium (100 mg), or a corresponding quantity of powder from capsules, in dimethylformamide (50 ml) and apply to a column of Amberlite IRC-50 (H^+ form) (10 g) which has been soaked in dimethylformamide. Elute with the same solvent and titrate the first 75 ml of eluate with 0·1 *N* Na methoxide in benzene - methanol to a

visual end-point (azo violet indicator) or potentiometrically. The results agree well in accuracy and precision with those by the U.S.P. method for the pure material. It is thought that the U.S.P. method gives low results with capsules. A. R. ROGERS

3745. **Fluorimetric assay for minute amounts of some thiohydantoins.** M. E. Auerbach and E. Angell (Anal. Lab., Sterling-Winthrop Res. Inst., Rensselaer, N.Y., U.S.A.). *J. Pharm. Pharmacol.*, 1958, **10** (12), 776–779.—This method has been applied to the determination of 5-*n*-heptyl-2-thiohydantoin and related compounds in urine, plasma and spinal fluid. *Procedure*—Mix the sample, containing $\simeq 1$ μg of thiohydantoin, with phosphate buffer of pH 6·0 (2 ml), dilute to 5 ml with H_2O and shake for 2 min. with $CHCl_3$ (8 ml). Withdraw 5 ml of the $CHCl_3$ layer, evaporate to dryness, cool and dissolve the residue in *iso*propyl alcohol - *iso*butyl alcohol (3:1) (4 ml). Add H_2O (2 ml), aq. NH_3 - NH_4Cl buffer of pH 10·2 (0·5 ml) and a 2% soln. of dichlorobenzoquinonechlorimine in *iso*propyl alcohol (0·5 ml) and after 2 hr. measure the fluorescence in a Coleman fluorimeter with B-1 primary and P-C-1 secondary filters.
A. R. ROGERS

3746. **Separation and colorimetric determination of *p*-aminobenzoic acid in procaine.** Shih-Jee Jow and Kuen Lung (Dept. of Pharm., Second Military Med. Coll., Shanghai). *Acta Pharm. Sinica*, 1959, **7** (1), 6–9.—*p*-Aminobenzoic acid (**I**) may be extracted satisfactorily with diethyl ether from aq. soln. of procaine at pH 3·6, K H tartrate being used as a buffer. The extract is evaporated to dryness and **I** in the residue is treated with 6 *N* acetic acid (5 ml) and 2% *p*-dimethylaminobenzaldehyde in ethanol (2 ml) (*cf.* Tanber, *J. Amer. Chem. Soc.*, 1941, **63**, 1488). The soln. is diluted to 25 ml with water and the yellow colour developed is measured after 1 hr. in a photometer at 458 mμ. The colour is stable for at least 1 week. Beer's law is obeyed in the range from 10 to 100 μg of **I**. S. H. YUEN

3747. **Separation and quantitative determination of phenylbutazone (4-*n*-butyl-1:2-diphenylpyrazolidine-3:5-dione) in pharmaceutical preparations.** M. Deffner and A. Issidorides-Deffner (Lab. de Contrôle et de Rech. de la Vitarine Greece Co., Cholargos-Athènes, Greece). *Chim. Anal.*, 1958, **40** (12), 460–462.—Phenylbutazone (**I**) gives a coloured complex with $FeCl_3$ and 2:2′-dipyridyl (**II**), which is measured spectrophotometrically. Treat 1 ml of test soln. (containing 0·25% of **I** in abs. ethanol) with 1 ml of 0·25% abs. ethanolic $FeCl_3.6H_2O$ (**III**) and 1 ml of 0·5% abs. ethanolic **II**. Make up to 25 ml with abs. ethanol and read the extinction at 520 mμ, 20 min. after the addition of **III**. A blank should be treated similarly and, as the extinction rises rapidly with time, and the rate falls off after 15 to 20 min., a known soln. should be similarly treated. The method is suitable for concn. of **I** from 5 to 30 μg per ml. For compressed tablets, several are powdered and a suitable aliquot is suspended in water and extracted with benzene, the extract being made up to a known vol. with benzene and an aliquot diluted with abs. ethanol to give 0·025% of **I**, and analysed as above. Similar extraction after acidification with HCl will give **I** combined as the Na or Ca salt. Results agree well with those by the B.P.C. gravimetric method, but results by measurement of the Na salt at 264 mμ are distinctly higher. Separation of **I** from other substances easily oxidised by $FeCl_3$ is achieved by chromatography, either on plain paper with butanol - water, or on paper treated with 50% formamide in acetone or 2·5% petroleum jelly in ether, with $CHCl_3$ or $CHCl_3$ - benzene as solvent, the spray reagent being a mixture of **III** and **II**, or Ehrlich reagent. R. E. ESSERY

3748. **Vanadametry. Assay of *iso*nicotinic acid hydrazide [isoniazid].** H. S. Gowda and G. G. Rao (Chem. Lab., Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1959, **165** (1), 36–38 (in English).—Isoniazid (**I**) is rapidly and quant. oxidised by 0·05 *N* $Na_4V_2O_4$ in 8 *N* H_2SO_4 and may be determined by the back-titration of an added excess with standard $(NH_4)_2SO_4.FeSO_4$ soln. Excipients (lactose, glucose and starch) do not interfere. Results agree to within ±0·5% and 5%, respectively, with the results of bromimetric and iodimetric determinations of isoniazid and Rimifon tablets, respectively. *Procedure*—Weigh 20 tablets and crush finely. Dissolve a portion containing 0·3 to 0·4 g of **I** in water, filter, and dilute to 250 ml. To a 10-ml aliquot add 0·05 *N* $Na_4V_2O_4$ (20 ml) and 20 *N* H_2SO_4 (20 ml). After 1 min., back-titrate the excess of $Na_4V_2O_4$ with standard $(NH_4)_2SO_4.FeSO_4$ soln., with N-phenylanthranilic acid as indicator.
J. P. STERN

3749. **Determination of isoniazid methanesulphonate.** Masayoshi Tatsuzawa (Nat. Hygienic Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *Japan Analyst*, 1958, **7** (12), 790–792.—The oxidation titration of isoniazid methanesulphonate (**I**) with KIO_3 or $KBrO_3$ (*cf.* Kühni *et al.*, *Anal. Abstr.*, 1955, **2**, 1911) was examined with reference to the effect of starch, lactose and carboxymethylcellulose. The removal of SO_2 is completed by heating with dil. HCl for 5 min. There is no interference from the carbohydrates and formaldehyde produced by the hydrolysis of **I**. The sample (0·1 g) is dissolved in water (10 ml), boiled with 4 *N* HCl (10 ml) for 5 min., mixed with conc. HCl (20 ml) and 5 drops of 0·2% indigo carmine and titrated with 0·025 *N* KIO_3 or 0·1 *N* $KBrO_3$. K. SAITO

3750. **Potentiometric determination of Artane [benzhexol] in non-aqueous solutions.** S. Negriţescu-Arizan. *Rev. Chim., Bucharest*, 1958, **9** (11), 627–629.—A differential titration method is used. First the free amine present as impurity is determined, and then the mixture of the benzhexol hydrochloride (**I**) with the Mannich base hydrochloride (**II**) (another impurity). *Procedure*—The sample (0·2 g) is dried at 105° and dissolved in warm glacial acetic acid (7 to 8 ml). After cooling it is titrated potentiometrically with $HClO_4$ (0·1 *N*) to the end-point (= *n* ml). To this soln. 4·3 ml of a soln. of mercuric acetate (5% in glacial acetic acid) is added, and the mixture is re-titrated. If *N* ml is the total titre, then $(N - n)$ is the vol. (ml) of titrant equiv. to **I** plus **II**. A graph is used to determine the percentage of **I** in the mixture. It is claimed that the analysis requires only 30 min., and that errors do not exceed ±2%. H. SHER

3751. **Determination of phenolic compounds in pharmaceutical preparations using 4-aminophenazone.** C. A. Johnson and R. A. Savidge (Standards Dept., Boots Pure Drug Co. Ltd., Nottingham, England). *J. Pharm. Pharmacol.*, 1958, **10**, Supplement, 171T–181T.—Conditions affecting the method of determination of phenols based upon coupling with 4-aminophenazone in the presence of an alkaline oxidising agent have been examined and the importance of a rigid control of pH stressed. The

reactivity of many phenols of pharmaceutical interest has been investigated and the application of the method to a number of pharmaceutical preparations is described. A. R. ROGERS

3752. **Complexometric determination of rivanol [ethacridine lactate].** L. Przyborowski (Dept. of Pharm. Chem., Medical Acad., Lublin, Poland). *Acta Polon. Pharm.*, 1959, **16** (1), 31–34.—An indirect complexometric method for the determination of ethacridine lactate (**I**) is described, together with procedures for commercial grades and pharmaceutical preparations. It is based on pptn. of **I** from an aq. soln. with a standard soln. of CdI_2. The ppt. $(C_{13}H_{13}ON_3)_2H_2.CdI_4$ so formed is insol. in water containing KI. Excess of CdI_2 in the filtrate, buffered with hexamine, is determined complexometrically, with xylenol orange as indicator. The method, which takes <30 min., is useful for batch determinations of substance, soln. and tablets. Dilute aq. soln. of **I** used in medical prep. are best adjusted to contain 0·05 to 0·2 g, and in tablets (usually containing 0·1 g) the error is $\gtrless 1\%$, after correcting for the solubility of the ppt.
W. B. MIASKOWSKI

3753. **Methods for the determination of benzethonium chloride (Phemerol chloride).** D. M. Patel and R. A. Anderson (Parke, Davis & Co., Detroit, Mich., U.S.A.). *Drug Standards*, 1958, **26** (6), 189–193.—To a soln. of benzethonium chloride (300 mg) in H_2O (75 ml) add 0·05% bromophenol blue soln. (0·4 ml), $CHCl_3$ (10 ml) and *N* NaOH (1 ml) and titrate with 0·02 *M* Na tetraphenylboron, with shaking. The $CHCl_3$ layer changes from blue to colourless at the end-point. The recovery in 8 replicate determinations ranged from 100·1% to 100·4%. The following gravimetric procedure is of comparable accuracy and precision and may be applied to products that contain a dye that interferes with the visual end-point of the titrimetric method. To a soln. of benzethonium chloride (150 mg) in 60% ethanol (50 ml) add 2·5% Na tetraphenylboron soln. (10 ml), with continuous gentle stirring, set aside overnight, filter through sintered glass, wash the collected ppt. with H_2O and weigh it after drying at 105° for 2 hr. A. R. ROGERS

3754. **Quantitative polarographic determination of 'Mercurit'.** N. Z. Bruja. *Rev. Chim., Bucharest*, 1958, **9** (12), 685–688.—The method outlined for 'Mercurit' [the sodium salt of N-(3-hydroxymercuri-2-methoxypropyl)phthalamic acid] is claimed to be suitable for similar mercuric compounds. The most suitable electrolyte is a mixture of 16 g of KCl and 12 g of citric acid per 100 ml; the pH should be between 3 and 5·5, when the value of $E_{\frac{1}{2}}$ becomes $-0{\cdot}35$ V. Oxygen must be removed by bubbling CO_2 through 10 ml of the test soln. for 5 min. *Procedure*—The 'Mercurit' soln. (0·0025 *M*) (1·4 ml) is treated with 38·6 ml of water and diluted to 100 ml with the basal electrolyte. A 5-ml aliquot is taken, O is removed and the polarographic determination is carried out, the result being compared with a standard. The max. error is claimed to be $\pm 1\%$. H. SHER

3755. **Polarographic properties of nitro derivatives of 2-aminothiazole. I. Quantitative polarographic determination of 2-amino-5-nitrothiazole, and its acetyl and formyl derivatives.** A. Danek and M. Eckstein (Dept. of Inorg. and Anal. Chem., Med. Acad., Kraków). *Acta Polon. Pharm.*, 1959, **16** (1), 13–20.—2-Amino-5-nitrothiazole and its acetyl and formyl derivatives undergo reduction on the dropping mercury electrode in the presence of water - ethanol - KCl, giving 2-step reduction curves. The results show that all three preparations can be determined by this method at pH 1 to 12, and that for analytical purposes the application of buffer soln. is unnecessary as the curves are well developed in the ethanolic aq. soln. of KCl with the addition of gelatin. This method can be used for concn. of $\simeq 10^{-5}$ *M*. The height of the curves is linearly proportional to the concn. of the compound. The method can also be applied to the determination of 2-amino- and 2-acetamido-5-nitrothiazole in pharmaceutical preparations.
W. B. MIASKOWSKI

3756. **Isotope-labelled cancerostatic and bacteriostatic agents. I. Synthesis of [4:5-^{14}C]azauracil and [4-^{14}C]azathymine.** J. Morávek (Res. Inst. of Radiol., Prague). *Chem. Listy*, 1958, **52** (11), 2147–2152.—A radiochromatographic method has been found suitable for controlling intermediates and isolated products in the synthesis of 6-[4:5-^{14}C]-azauracil and 6-[4-^{14}C]-azathymine. The method has been carried out by a descending technique on Whatman No. 4 paper, with *n*-butanol saturated with H_2O as solvent. The detection is by means of an apparatus in which the chromatograms are continuously passed across a Geiger - Müller tube and the activity is automatically registered. The use of various chemical detecting agents is described. The following compounds have been studied—oxalic acid (R_F 0·0) (detection with bromocresol green), glyoxylic acid (R_F 0·73) (detected with bromocresol green or dinitrophenylhydrazine), the thiosemicarbazone of glyoxylic acid (R_F 0·59), thioazauracil (R_F 0·61) (detected with u.v. light, with dinitrophenylhydrazine or Ag_2CrO_4), the thiosemicarbazone of pyruvic acid (R_F 0·73), thioazathymine (R_F 0·75) (detected in u.v. light with Ag_2CrO_4), and azathymine (R_F 0·59). J. ZÝKA

3757. **Direct assay of fatty acid in the presence of its zinc salt in anti-fungal preparations.** D. E. Dean and R. J. Hackman (Anal. Development Lab., Shulton Inc., Clifton, N.J., U.S.A.). *Drug Standards*, 1958, **26** (6), 194–198.—The free acid is extracted with light petroleum and determined by non-aqueous titration. The results agree with those by the method of "New and Nonofficial Remedies," 1953 (Tests and Standards, p. 317), but are of much greater precision. *Procedure*—For a sample of anti-fungal powder, stir an amount containing $\simeq 0{\cdot}8$ milli-equiv. of free acid with light petroleum (4×15 ml) in a sintered-glass funnel and filter under gentle suction. For a sample of anti-fungal ointment, mix an amount containing $\simeq 0{\cdot}8$ milli-equiv. of free acid with Na_2SO_4 (2 g), shake with light petroleum (3×20 ml) and centrifuge to effect separation of the phases. Dilute the combined extracts with acetone (60 ml) and titrate potentiometrically (antimony electrode and methanol-modified S.C.E.) with 0·1 *N* tetrabutylammonium hydroxide. Perform a control determination to compensate for the acidity of the acetone and for the CO_2 absorbed during the extraction.
A. R. ROGERS

See also Abstracts—**3375**, Reagent for alkaloids. **3480**, Determination of Cr in sutures. **3556**, Determination of formyl and acetyl groups in digitalis glycosides. **3657**, Determination of colchicine. **3658**, Determination of phenylethylbiguanide. **3660**, **3661**, Determination of azovan

blue. **3676**, Determination of catechin in catechu. **3770**, Diastatic power of malt extract. **3805**, Precision in pharmaceutical analysis. **3806**, Measurement of density of liquids. **3823**, Chromatography of quaternary ammonium compounds. **3843**, Determination of prednisolone.

Food

Food and food additives, beverages, edible oils and fats, vitamins.

3758. **Determination of the apparent purity of beet sugar factory juices and syrups. I.** W. H. Parker (British Sugar Corp., Ltd., 134 Piccadilly, London, England). *Int. Sugar J.*, 1958, **60** (720), 355–357.—The apparent purity of a juice or syrup is defined as the polarisation per 100° Brix. The sample (100 ml) is measured into a 100/110 ml flask and basic Pb acetate is added for clarification, the whole is made up to 110 ml, mixed and filtered, and the direct polarisation is taken in a 20-mm tube, a saccharimeter of 26 g normal weight being used. Then, if S is the sugar (%), P the polarisation, B the ° Brix of the sample and D its sp. gr., all at 20°, then $S = (0{\cdot}26 \times 1{\cdot}1 \times P)/(0{\cdot}99718 \times D)$, and purity $= 100S/B = 28{\cdot}6P/0{\cdot}99718BD$. Factors for the expression $28{\cdot}6/0{\cdot}99718BD$ can be calculated for various values of B, and then log purity = log P + log factor. A slide-rule can then be constructed from which, given P and B, the purity can be read. The construction of such a rule, 2 ft. long and covering the range 12° to 16° Brix, is described, purity being readable to 0·1%.

R. E. Essery

3759. **Studies on the determination of sugars in molasses, especially on the comparison of the Bertrand method and the Lane method, and the determination of unfermentable reducing sugars, varying the condition of inversion.** K. Okano and T. Kosaka. *Proc. Res. Soc. Japan Sugar Refineries' Technologists*, 1958, **7**, 51–64.—The two methods of analysis were investigated for soln. with different sugar and HCl concn., different inversion times or Pb acetate additions to sucrose soln. or molasses. Conclusions reached were—in sucrose soln. or molasses (each with 10% of sugars), nearly equal values for the reducing sugar content after inversion were obtained by either method, and the concn. of HCl or sugar did not affect the results; the use of lead clarifying agents, either before or after inversion, resulted in low values, the discrepancy being greater with larger amounts of lead reagent, and more with the Bertrand method than with the Lane method; the results with inverted molasses were irregular, soln. with $\simeq$25% of sugar showed the highest reducing values, and the Bertrand method gave higher figures. With larger amounts of HCl for inversion, more unfermentable sugars seemed to be produced. Sugar Ind. Abstr.

3760. **Simplified method of protein determination in cereals and cereal products.** J. Janicki, E. Kaminski and R. Ozog (Inst. für Getreideforsch., Warszawa, Poland). *Getreide*, 1958, **8** (12), 89–90.—The use of boiling-tubes, instead of flasks, for Kjeldahl digestions is described. These are held in a specially designed duralumin block which is heated either electrically or by gas. In the distillation process the ammonia is distilled into 2% boric acid and titrated directly, with a mixture (5:1) of bromocresol green and methyl red as indicator.

J. V. Russo

3761. **Estimation of the total solids and solids-not-fat of milk from the density and fat content.** S. J. Rowland and A. W. Wagstaff (Nat. Inst. Res. Dairying, Shinfield, Reading, England). *J. Dairy Res.*, 1959, **26** (1), 83–87.—The accuracy of the method specified in British Standard 734:1937 is assessed on 2425 samples (in five series over different years) against the gravimetric method. The percentages of solids by the density method were lower by an average of 0·06 than those determined gravimetrically. To correct for this error and to compensate for the lower, more accurate fat percentages arising from the recent reduction in the Gerber milk pipette, the following modified formulae are proposed—$T = 0{\cdot}25D + 1{\cdot}22F + 0{\cdot}72$, and S.N.F. $= 0{\cdot}25D + 0{\cdot}22F + 0{\cdot}72$. These formulae were adopted in October 1957, in an amendment to the B.S. 734 published in 1955. W. H. C. Shaw

3762. **Direct determination of citric acid in milk with an improved pyridine - acetic anhydride method.** J. R. Marier and M. Boulet (Nat. Res. Council, Ottawa, Canada). *J. Dairy Sci.*, 1958, **41** (12), 1683–1692.—A study is made of the reaction conditions at temp. from 17° to 60°. The recommended method can be applied directly to diluted milk (after centrifuging or diluting and filtering), to milk serum and, with a correction for interference by fat, to homogenised milk. A correction is also required if trichloroacetic acid is used in preparing the serum. *Procedure*—To 1·0 ml of sample containing 25 to 200 μg of anhydrous citric acid add 1·30 ml of pyridine. Swirl briskly, add 5·70 ml of acetic anhydride, swirl again and place in a water bath at 32° $\pm$ 0·25°. After 30 min. cool and measure the extinction at 420 mμ within 30 min. against a blank prepared with 1·0 ml of water instead of the sample. The curve is rectilinear up to 200 μg of citric acid.

W. H. C. Shaw

3763. **Colorimetric determination of available lysine in milk.** Susumu Adachi and Takeo Nakanishi (Fac. of Agric., Tohoku Univ., Kitarokubancho, Sendai). *J. Agric. Chem. Soc. Japan*, 1958, **32** (9), 728–732.—The reaction between the ϵ-amino group of lysine and 1-fluoro-2:4-dinitrobenzene (**I**) (Carpenter and Ellinger, *Biochem. J.*, 1955, **61**, xi) was applied to the determination of lysine. The extinction of ϵ-dinitrophenylated lysine (**II**) at 455 mμ is proportional to the concn. for $<$3 mg of the hydrated hydrochloride of **II** per 100 ml. On extraction with diethyl ether, **II** remains in the aq. phase with other dinitrophenylated products. *Procedure*—Dissolve $NaHCO_3$ (100 mg) in the sample of milk (0·5 ml), add **I** in ethanol (2·5%) (2 ml) and set aside in the dark for 2 hr. Expel the ethanol, add HCl (6 *N*) (5 ml), seal the tube and keep at 105° for 15 min. Filter the product, dilute to 10 ml and shake a 2-ml aliquot with ether (2 $\times$ 10 ml). To 1 ml of the aq. layer add 5% acetic acid (0·7 ml) and *N* NaOH (2·7 ml) to adjust the pH to 4·5, make up to 10 ml and measure the extinction.

K. Saito

3764. **Reaction of lactose with anthrone and its application to the estimation of lactose in casein and other dairy products.** E. L. Richards (Dairy Res. Inst., Palmerston North, New Zealand). *J. Dairy Res.*, 1959, **26** (1), 53–57.—For the rapid and accurate determination of lactose in casein a modification of the anthrone reaction is recommended. *Reagent*—Dissolve 150 mg of anthrone in 70% v/v H_2SO_4 (98% w/w) to 100 ml. Cool and store for $<$2 hr. (preferably overnight) at 0°. *Procedure*—Place

1 g of casein and 0·1 g of $NaHCO_3$ in a large boiling-tube. Add 25 ml of water, warm and stir in a bath at 60° to 70° until the casein has dissolved (10 to 15 min.). Add with stirring 25 ml of 0·1 *N* H_2SO_4 and filter. Place 1 ml of filtrate (≯100 μg of lactose) in a boiling-tube immersed in an ice bath. Add, with shaking, 10 ml of ice-cold anthrone reagent. Stopper the tube, mix and place in a boiling-water bath for 6 min. Cool in an ice bath for 30 min. then read the extinction at 625 mμ. Use 1 ml of water for the blank and calibrate by including a standard (100 μg) with each batch of analyses The curve is rectilinear. For milk, dilute 1 ml of sample to 500 ml with water and take 1 ml for assay.

W. H. C. SHAW

3765. **Determination of NN′-diphenyl-*p*-phenylenediamine (DPPD) in milk by paper chromatography.** B. A. Dehority (Storrs Agric. Exp. Sta., Conn., U.S.A.). *J. Chromatography*, 1959, **2** (1), 81–83.—The difficulty arising in the determination of NN′-diphenyl-*p*-phenylenediamine (**I**) in milk due to the insolubility of part of the non-saponifiable fraction in an acetone - HNO_3 mixture can be overcome by paper chromatography. Soln. of **I** in benzene are chromatographed with 80% aq. methanol. A band between R_F 0·70 and 0·85 is cut out and shaken with conc. HNO_3, and the extinction at 490 mμ is measured. With pure benzene soln. of **I** the recovery is 95·8%. Recovery of **I** added to milk before the extraction of the non-saponifiable fraction is 51·44% ± 3·85 (8 determinations).

G. BURGER

3766. **Detection of butylated hydroxytoluene in lard.** J. Wurziger and R. Pohlmann (Chem. u. Lebensmitteluntersuchungsanst., Hygien. Inst., Hamburg). *Dtsch. LebensmittRdsch.*, 1958, **54** (12), 307–308.—The method is based on the production of ether-soluble coloured substances when butylated hydroxytoluene (**I**) is treated with ethanolic KOH or powdered $Ca(OH)_2$. These coloured compounds show a strong and sharp absorption maximum at 368 mμ. *Procedure*—Lard (5 g) is saponified for 30 min. with 25 ml of *N* ethanolic KOH. Water (25 ml) is added and the mixture extracted with diethyl ether (2 × 50 ml). The ether soln. is washed with water (3 × 10 ml), dried with anhyd. Na_2SO_4 for 15 min., and evaporated. The residual unsaponifiable material is then heated with 10 ml of *N* ethanolic KOH for 10 min. on a boiling-water bath. On cooling, a red to tan colour appears in the presence of **I**. The method will detect 0·005% of **I** (0·25 mg in 5 g of lard), and can be made quant. by comparison with standards similarly treated. Gallates, nordihydroguaiaretic acid, butylated hydroxyanisole and fat oxidation products do not interfere, as the coloured compounds formed from these are insoluble in ether. E. C. APLING

3767. **Determination of sugars in fruits. I. Effect of conditions of hydrolysis on the determination of sucrose.** Kazuo Osodo, Hidejiro Kazumi, Masayuki Kotaka and Hanao Shitomi (Instruction Inst. of Rural Ind., Numata, Shinjo, Yamagata-ken). *J. Agric. Chem. Soc. Japan*, 1958, **32** (9), 671–673.—For the hydrolysis of sucrose in fruits containing 60 to 70% of fructose in the total sugar, the following conditions were suitable—0·1% HCl, 20 to 30 min. in a boiling-water bath; 2·4% HCl, 8 to 16 hr. at 30°, or 4 to 8 hr. at 40°, or 45 to 60 min. at 50°. No appreciable decomposition of fructose was observed. The determination of invert sugar was effected by Somogyi's method (*J. Biol. Chem.*, 1933, **100**, 695).

K. SAITO

3768. **Determination of o-hydroxydiphenyl in oranges.** W. Thole (Bundesgesundheitsamt, Max von Pettenkofer Inst., Abt. f. Physiol., Pharmakol. u. Arzneimittelwesen, Berlin-Dahlem, Germany). *Z. LebensmittUntersuch.*, 1959, **109**, 40–43.—*Procedure*—Mix the sample (200 g) with water (500 ml) and H_3PO_4 (5 ml), and steam-distil into a receiver containing 500 ml of water. Extract the distillate (1 litre) with *cyclo*hexane (3 × 50 ml). Extract the preservative from the *cyclo*hexane into 0·1 *N* NaOH (10 × 15 ml), make up the extracts to 150 ml with 0·1 *N* NaOH, and (within 1 hr.) make up 20 ml of the soln. with a borate buffer at pH 10·4 (3·15 ml) and 0·1 *N* NaOH to 50 ml. To this soln. add (without delay) a 2% aq. soln. of 4-aminophenazone (0·5 ml) and 2% aq. $K_3Fe(CN)_6$ (1 ml), and measure the colour at 510 to 520 mμ in comparison with the colour obtained from standard soln. of the preservative. Maximum errors are +3% and −7%.

P. S. ARUP

3769. **Phenolic constituents of *Prunus domestica*. I. The quantitative analysis of phenolic constituents.** T. Swain and W. E. Hillis (Div. of Forest Products, C.S.I.R.O., Melbourne, Australia). *J. Sci. Food Agric.*, 1959, **10** (1), 63–68.—Gum in the flesh of canned plums may be related to the transport of phenolic glycosides from the kernels; methods for determining these are discussed. *Total phenols*—Dilute an aliquot of sample soln. (containing ≯0·5 ml of alcohol) with H_2O to 7 ml in a 10-ml tube. Add 0·5 ml of Folin - Denis reagent and shake. Add 1 ml of satd. Na_2CO_3 soln. 3 min. later, and dilute to 10 ml. Measure the extinction at 725 mμ after 1 hr. against a H_2O - reagent blank. *Leucoanthocyanins*—Place 1 ml of sample soln. (≯50% of alcohol) in each of two tubes (6 in. × 1 in.) and add 10 ml of reagent (25 ml of conc. HCl diluted to 500 ml with *n*-butanol). Shake and place one tube in a water bath at 97° ± 1°. After 3 min., stopper the tube and heat for a further 37 min.; remove the stopper and cool the tube in H_2O for 5 min. Measure the extinction at 550 mμ (also at 650 mμ if chlorophyll is present) against the contents of the unheated tube. *Flavanols*—Place aliquots (containing ≯0·1 ml of methanol) in two 25-ml flasks, *A* and *B*. Add 4 ml of fresh reagent (1% vanillin in 70% v/v H_2SO_4) to *A* and 4 ml of 70% H_2SO_4 to *B*, keeping the temp. ≯35°. After 15 min. measure the extinctions of *A*, *B* and a blank *C* (4 ml of reagent plus 2 ml of H_2O) at 500 mμ against 47% H_2SO_4. Subtract readings for (*B* + *C*) from *A*. *Anthocyanins*—Place 3 ml of HCl (0·5 *N* in 80 to 85% v/v methanol) in each of 2 tubes. Dilute one with 1 ml of HCl in methanol (5:1 v/v, 3 *N*) and add 1 ml of reagent (1 ml of 30% H_2O_2 in 9 ml of 3 *N* HCl in methanol, 5:1 v/v) to the tube containing the sample. Set aside in the dark for 15 min. and measure the extinction at 525 mμ, with the first tube as a blank.

P. D. PARR-RICHARD

3770. **Determination of the diastatic power of malt and malt extract.** S. Gerardis. *Birra e Malto*, 1958, Nov., 24–28.—A method slightly modified from that of Pollak and Egloffstein is recommended. Test extracts of malts were prepared by extracting 10 g of finely ground malt (or 5 g of malts of high diastatic power) with 160 ml of water at 40° for 30 min., then cooling to 18° to 20°, making up to 200 ml and filtering. Malt extract (10 g) was dissolved in warm water and the soln. cooled to 18° to 20° and made up to 200 ml. Starch paste for conversion was prepared fresh daily by stirring a slurry of 9 g of arrowroot starch (10 to 15% of

moisture) in a little water into 250 ml of water at 90° to 95°. After being stirred at this temp. for 30 min., the paste was cooled to 18° to 20° and made up to 300 ml; 50 ml was removed and 3 ml of acetate buffer (pH 4·7) was added to the remaining 250 ml. For saccharification, 250 ml of the buffered starch paste was incubated with 4 ml of test extract at 37·6° for precisely 30 min., when the reaction was stopped by the addition of 10% KOH soln. (3 ml). The mixture was cooled to 18° to 20° and made up to 300 ml. The maltose content of this conversion liquid was determined by titration with Fehling's soln. (5 ml each of reagents *A* and *B*, diluted with 60 ml of water). Results were calculated as indicated by Muntoni (*J. Inst. Brew.*, 1958, 431).

ABSTR. J. INST. BREW.

3771. **Paper-chromatographic determination of L(+)-ascorbic acid in beer.** H. R. Stocker. *Schweiz. Brauerei Rdsch.*, 1958, **69** (12), 211–213.—Ascorbic acid (**I**) can be separated from other reducing substances with *n*-butanol - water - acetic acid (4:1:1) as ascending solvent, in an atmosphere previously saturated with the solvent vapour, and located by spraying with 2:6-dichlorophenolindophenol (**II**) in 50% ethanol. The requisite amount of test sample may reach 0·4 ml. A soln. of **I** in aq. 0·5% metaphosphoric acid is used as a standard for comparison in parallel runs. The corresponding unsprayed spots are cut out and eluted with 3% aq. oxalic acid, 1 to 5% aq. metaphosphoric acid, or methanol. The determination can be made by titration of the eluate with 0·001 *N* **II**, or (preferably) by spectrophotometric measurement of the coloration produced on admixture with a soln. of **II** under specified conditions. P. S. ARUP

3772. **Determination of the humulone of hops by conductimetric titration.** J. de Clerck and J. Jerumanis. *Bull. Ass. Éc. Brass., Louvain*, 1958, **54**, 249–253.—Extraction of hops by means of hexane before conductimetric titration as recommended by Hartong *et al.* (*Int. Tijdschr. Brouw. Mout.*, 1956–1957, 15) yields low results. In the present method, extraction is effected in a blender with methanol, and the resins are transferred to hexane as in the gravimetric Walker-Hastings determination as modified by de Clerck (*Cours de Brasserie*, Van Linthout, Louvain, 1948, Vol. 2, p. 210). The humulone is then determined by conductimetric titration. An aliquot (100 ml) of the hexane soln. is concentrated to 10 ml, methanol (20 ml) is added and the soln. is washed into a conductivity cell with methanol (2 × 10 ml). The soln. is titrated with 4% Pb acetate soln., and the required vol. of this soln. multiplied by a factor of 1·524 gives the percentage of humulone in the hops. The precision of the method compares favourably with that of the gravimetric method in the analysis of hops containing 4 to 7% of humulone, and is superior in the analysis of old hops containing <1·5% of humulone. ABSTR. J. INST. BREW.

3773. **Determination of tartaric acid in wine.** W. Diemair and G. Weinberger (Univ. Inst. f. Lebensmittelchem., Frankfurt a. Main, Germany). *Z. LebensmittUntersuch.*, 1959, **109** (1), 34–40.—The accuracy of the micro-method of Gorbach and Vaupotitsch (*cf. Anal. Abstr.*, 1957, **4**, 3130) decreases considerably as the amount of tartaric acid present in the sample falls below 100 mg per litre. In such cases the results are greatly influenced by the amount of washing undergone by the pptd. K H tartrate. P. S. ARUP

3774. **Paper-chromatographic studies on fats.** M. Jáky (Forschungsinst. f. Pflanzliche Öle, Budapest). *Fette, Seif., Anstrichmitt.*, 1959, **61** (1), 6–10.—The R_F values of fatty acids were determined by the chromatography of known mixtures and used in the analysis of fatty acid mixtures from the seed oils of sunflower, poppy, cotton and maize. The separated acids were quant. determined by a micro-titration procedure, which is described. In all cases considerable amounts of linoleic acid were present in addition to oleic acid. Monoglycerides have been separated by eluting with acetone and developing the spots with a 0·05% aq. soln. of Rhodamine B (C.I. Basic Violet 10), and quant. determined by measuring the size of the spots. Results are satisfactory and the determination can be completed in ≃2 hr. Unsaponifiable material can be analysed by chromatographing a 1% soln. of the extracted fraction in light petroleum (boiling-range 190° to 210°), eluting with ethanol - *iso*propyl alcohol - water (20:2:3) satd. with light petroleum, and developing with Rhodamine B or $KMnO_4$ soln. α-Tocopherol is present in all the oils examined, and other tocopherols and sterols have also been identified. Results are tabulated. By eluting in several stages, separation of a neutral oil containing triglycerides into 4 fractions was achieved. The fractions were then saponified and the fatty acid mixtures chromatographed. Trilinolein and glycerides of oleic and linoleic acids have been shown to be present in sunflower-seed oil, and glycerides of erucic and stearic acids in rape-seed oil. S. M. MARSH

3775. **Revision of "Standard testing methods for the fats and waxes industry". XXVIII. Analysis of waxes and wax products.** A. Seher and G. von Rosenberg (Dtsch. Inst. f. Fettforschung, Univ. Münster, Westfalen). *Fette, Seif., Anstrichmitt.*, 1959, **61** (1), 17–20.—This is Report No. 38 of collaborative work undertaken under the auspices of the Deutsche Gesellschaft für Fettwissenschaft. Full details, with diagrams of apparatus, are given for the recommended procedures for sampling, and the determination of alkali number, water content, and normal paraffin content of waxes. A method is also given for the determination of acetone-soluble matter in montan wax. S. M. MARSH

3776. **Colorimetric determination of urease activity in soya-bean oil.** G. Schramm and P. D. Aines (Procter & Gamble Co., Cincinnati, Ohio, U.S.A.). *J. Amer. Oil Chem. Soc.*, 1959, **36** (1), 1–3.—To 1 g of meal is added 50 ml of a urea soln. (0·4 ± 0·0005 g of urea dissolved in 1 litre of a buffer soln. prepared from 22·3 g of $Na_4P_2O_7.10H_2O$ in 980 ml of water and 3 ml of HCl; the pH is adjusted to 7·7 to 7·8), and the mixture is heated at 40° for 30 min., with shaking every 5 min. The soln. is then removed from the source of heat and 0·5 ml each of conc. HCl, ferrocyanide soln. [10·6 g of $K_4Fe(CN)_6.3H_2O$ dissolved in 100 ml of water] and Zn acetate soln. (22 g of Zn acetate dihydrate dissolved in 3 ml of acetic acid and 100 ml of water) and 0·1 g of charcoal are added. After shaking for 15 min. the soln. is filtered, and 10 ml is diluted to 25 ml with water; 10 ml of this soln. is mixed with 10 ml of *p*-dimethylaminobenzaldehyde soln. (16 g in 1 litre of 95% ethanol and 100 ml of conc. HCl), and after shaking the mixture for 10 min. the extinctions of the test soln. and a reagent blank are measured at 430 mμ. The concn. of urea is determined by comparison with a standard curve, and the urease

activity is expressed as the amount of urea decomposed under the specified conditions.

G. R. WHALLEY

3777. **Paper chromatography of fats. XXIX. The quantitative analysis of fatty acid mixtures by means of the copper - mercury process.** H. P. Kaufmann and H. Schnurbusch (Inst. f. Pharm. u. Lebensmittelchem., Univ. Münster, Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (11), 1046–1050.—Saturated and unsaturated fatty acids and their esters can be determined by quantitative paper chromatography if undecane (*cf.* Kaufmann and Mohr, *Ibid.*, 1958, **60**, 165) is used as the stationary phase. The dried chromatograms are treated for 1 hr. with 2% mercuric acetate in 1% v/v acetic acid and washed for 4 hr. in H_2O. The dried chromatograms are sprayed with 0·1% ethanolic diphenylcarbazone. Artificial mixtures of arachidic, stearic, palmitic, myristic and lauric acids were quant. determined by the copper and above-described mercury methods using planimetry. Results by both methods agreed well. Good agreement was also obtained with a mixture of oleic, linoleic and linolenic acids. As Hg^{2+} react with the double bond and the carboxyl group and Cu^{2+} only with the latter, a combination of the two methods is suggested for the quant. separation of critical pairs (*e.g.*, linoleic and myristic acids). A formula for the calculation of the composition of such a mixture is given. Results for the analysis of the fatty acid content of a number of natural oils by the combined methods are given.

S. BAAR

3778. **Analysis of long-chain fatty acids by gas - liquid chromatography. Micro-method for preparation of methyl esters.** W. Stoffel, F. Chu and E. H. Ahrens, jun. (Rockefeller Inst., 66th Street and York Avenue, New York, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 307–308.—The following method for the preparation and isolation of the methyl esters from lipid mixtures eliminates the use of alkali and diazomethane, which may lead to isomerisation and pyrazoline formation. *Procedure*—Heat the esters (1 to 10 mg) with dry benzene (0·5 ml) and a 5% soln. of HCl in super-dry methanol (4 ml) under reflux at 80° to 100° for 2 hr. with shaking. Cool, add H_2O (9 ml) and extract with light petroleum (boiling-range 30° to 36°) (3 × 3 ml). Neutralise and dry the extracts over Na_2SO_4 - $NaHCO_3$ (4:1) for 1 hr. and evaporate to dryness at 40° under reduced pressure. Purify the residue by sublimation at 60° and at a pressure of 0·2 mm (Hg) for 1 hr.

A. R. ROGERS

3779. **Detection of certain brominated long-chain fatty acid esters by gas - liquid chromatography.** R. A. Landowne and S. R. Lipsky (Yale Univ. Sch. of Med., New Haven, Conn., U.S.A.). *Nature*, 1958, **182**, 1731–1732.—Chromatography of a brominated mixture of methyl stearate and methyl oleate (1:2) on an 8-ft. column of 60 to 80-mesh Celite 545 coated with 10% poly(diethylene glycol glutarate) at 205°, with argon as carrier gas, revealed the presence of three peaks in addition to that of unchanged stearate. The retention volumes of these new components, which are unidentified, are greater than those of the original esters.

A. R. ROGERS

3780. **Enzymatic determination of polyunsaturated fatty acids.** J. MacGee (Miami Valley Lab., Procter & Gamble Co., Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 298–302.—A rapid method for the quant. determination of total *cis*-methylene-interrupted polyene acids is described. As little as 5 μg of linoleic acid can be determined with good accuracy; the coeff. of variation for 20 determinations of the extinction coeff. of linoleic acid was 1·8%. *Procedure*—Prepare a soln. of the sample in 0·2 *M* borate buffer of pH 9·0; esters must first be hydrolysed. Mix a 0·02% soln. of lipoxidase in 0·2 *M* buffer (0·1 ml) with a 3-ml aliquot, containing between 5 and 25 μg of free polyunsaturated fatty acids. Set aside at room temp. for 30 min. and measure the extinction at 234 mμ against a blank soln. prepared similarly but with use of boiled enzyme. The method has been applied to fats, oils, hydrogenated fats, fatty acids, esters, blood plasma, micro-organisms and plant seeds.

A. R. ROGERS

3781. **Gas - liquid chromatography of highly unsaturated fatty acid methyl esters.** W. Stoffel, W. Insall, jun., and E. H. Ahrens, jun. (Rockefeller Inst., New York, U.S.A.). *Proc. Soc. Exp. Biol. Med.*, 1958, **99** (1), 238–241.—Gas - liquid chromatography was carried out as described by James and Martin (*Biochem. J.*, 1956, **63**, 144) with an ionisation chamber detection method (*cf.* Lovelock, *Anal. Abstr.*, 1958, **5**, 3208), with the chamber vapour-jacketed at 197°. *Procedure*—Supply the mobile phase (argon) at a pressure of 170 mm (Hg). Pack each 4-ft. column with 5 g of acid-washed alkali-treated Celite 545 (140 to 200 mesh). Two stationary phases were studied, the non-polar vacuum grease Apiezon M and the polar polyester Reoplex 400. The Apiezon column contains 0·8 g of Apiezon and the Reoplex column 2 g of Reoplex 400. Condition both columns at 197° by flushing with N at 670 mm (Hg) for at least 3 days before analytical use. Calculate all relative retention volumes from apparent retention times (= time from the air peak to centre of the symmetrical elution peak). Recover the esters after chromatography by leading the effluent gas from the detector into a glass tube loosely packed with defatted cotton moistened with abs. ethanol. Proof is given that methyl esters of highly unsaturated long-chain fatty acids are not significantly altered in chemical structure during gas - liquid chromatography under the conditions given.

B. P. BLOCK

3782. **Improved iodimetric methods for the determination of lipid peroxides.** F. W. Heaton and N. Uri (Min. of Agric., Fisheries and Food Res. Estab., Greyhope Road, Aberdeen). *J. Sci. Food Agric.*, 1958, **9** (12), 781–786.—By de-aerating the test soln., errors due to induced oxidation are reduced; special reaction vessels are described. For the macro-procedure, take a sample containing ≤ 5 μmoles of peroxide, add 70 ml of a 2:1 mixture of glacial acetic acid and $CHCl_3$ and de-aerate continuously with pure N; follow the usual procedure and titrate with 0·002 *N* $Na_2S_2O_3$. The standard deviation is ±0·087 (4 determinations). For samples containing 0·02 to 5 μmoles, use 7·5 ml of de-aerated solvent; the total vol. including the KI soln. should be ≥ 10 ml. Measure the absorption at 370 to 500 mμ according to concn. (400 mμ for the concn. range 0·1 to 1·2 μmole of peroxide), excluding O throughout the test. The peroxide concn. can be determined in terms of either hydroperoxide or iodine by reference to the appropriate calibration curve.

P. D. PARR-RICHARD

3783. **Analytical detection of synthetic antioxidants in edible fats.** A. Seher (Dtsch. Inst. f. Fettforschung, Münster, Westf., Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (12), 1144–1153.—Tabulated results of the application of seven tests for the presence of 20 antioxidants in fat show the necessity for the application of at least three of the tests, namely the reactions with molybdophosphoric acid, ferric thiocyanate and ferric ferricyanide. Positive results are obtained with autoxidised oils (of peroxide value <10) in the absence of any antioxidant; negative results are, however, obtained after the removal of peroxides. Autoxidation products showing peroxide values >6 can similarly interfere with the determination of antioxidants by titration with ceric sulphate. When applying the Amer. Oil Chem. Soc. stability test to arachis oil, the time of heating at 105° should be prolonged to 8 hr. Spectrophotometric data are given for 10 antioxidants. For the isolation of antioxidants for spectrophotometric analysis, it is recommended to extract a soln. of the sample (20 g) in hexane (40 ml) with 75% methanol (2 × 30 ml), all operations being carried out in a current of inert gas.

P. S. ARUP

3784. **Photometric determination of vitamin D in presence of vitamin A.** M. Schmall, B. Senkowski, R. Colarusso, E. G. Wollish and E. G. E. Shafer (Anal. Res. Lab., Hofmann-La Roche Inc., Nutley, N.J., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (12), 839–844.—A basic method and three modifications are presented. Recovery experiments and a comparison of results with those obtained by bio-assay suggests that the method is accurate to about ±5%. *Procedure*—Saponify the sample, containing 4000 i.u. of vitamin D (**I**), and extract the unsaponifiable matter with light petroleum (boiling-range 30° to 60°). Transfer an aliquot to a column of Florex XXS and elute **I** with benzene. Carefully evaporate the eluate to dryness and dissolve the residue in $CHCl_3$. Allow an aliquot to react with the $SbCl_3$ reagent of Mulder *et al.* (*cf. Anal. Abstr.*, 1958, **5**, 998). Correct the extinction at 495 mμ by use of the colour inhibitor and method of calculation of Wilkie *et al.* (*cf. Anal. Abstr.*, 1959, **6**, 1538). Simultaneously perform a control determination of a known amount of **I** to which have been added vitamin A (**II**) and vitamin E in about the same amounts as are contained in the sample. For low-potency samples when interference is encountered with the basic method, mix the sample with water, saturate the soln. with crystalline sodium sulphate, extract with light petroleum, evaporate the extracts to dryness and apply the basic procedure to the residue. Alternatively, saponify, extract and purify on a column of Florex by the basic procedure, evaporate the benzene eluate to dryness, and apply a soln. of the residue in light petroleum to a column of Al_2O_3 containing 8% of water; remove degradation products of **II** by elution with benzene - light petroleum (3:1), then elute **I** with benzene and carry out the basic colorimetric procedure. For samples which contain a high proportion of **II**, saponify an amount of sample containing ≃7500 i.u. of **I**, and dissolve the unsaponifiable matter in the upper phase of a mixture of butanol - methanol - water - heptane (1:3:2:4). Apply the solution to a column of Hyfax polyethylene powder and develop with the lower phase of the solvent mixture. Remove the upper part of the column, which contains the **I**, and extract it with light petroleum. Then proceed with the chromatographic purification on Florex and colorimetry by the basic procedure. A. R. ROGERS

3785. **Studies on the microbiological assay of vitamins and amino acids by the pulp-disc method. I; II. The assay of several vitamins of the B group.** Hisao Ogawa, Yutaka Matsuya, Hiroko Ozawa, Makoto Kondo and Teijiro Uemura (Fac. of Agric., Tohoku Univ., Kitaroku-bancho, Sendai). *J. Agric. Chem. Soc. Japan*, 1958, **32** (1), 33–42.—The use of a sulphite pulp disc in place of a cup-plate was studied with biotin (**I**), pantothenic acid (**II**), nicotinic acid (**III**) (with *Lb. arabinosus* 17–5), pyridoxine (**IV**) (with *Sacch. carlsbergensis* ATCC 4228), and thiamine (**V**) (with yeast) (Sato *et al.*, *Ibid.*, 1957, **31**, 675). A sulphite pulp disc (diam. 11 mm) is impregnated with the sample soln. (0·05 ml), placed on Snell's medium (for **I**, **II** and **III**) (*J. Biol. Chem.*, 1941, **139**, 675) or Atkin's agar (1%) medium (for **IV** and **V**) (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 141), incubated at 37° for 12 hr. (for **I**, **II** and **III**) or at 30° for 14 hr. (for **IV** and **V**) and the diameter of the colony measured. The log of the concn. ∝ the diameter for 5 to 500 μg of **I** per ml, 0·5 to 50 μg of **II** and **III** and 0·05 to 5 μg of **IV** and **V**. The sensitivity is lower than the test-tube method but the variation (<5%) is less. The sterilised culture can be preserved for several weeks. No interference results from <20% of NaCl or Na_2SO_4.

III. Application to some vitamins and amino acids. Hisao Kojima and Yutaka Matsuya. *Ibid.*, 1958, **32** (2), 100–105.—This method was applied to 11 other vitamins and 18 amino acids with various bacilli and yeasts. Folic acid (0·01 to 1 μg per ml) and riboflavine are determined with *Lb. casei*, inositol (10 to 1000 μg) with *Sacch. carlsbergensis* and vitamin B_{12} (0·01 to 0·5 μg) with *Lb. leichmannii*. DL-α-Alanine (100 to 1000 μg per ml) is determined with *Lb. citrovorum*, L-arginine, DL-aspartic acid, L-cystine (25 to 2500 μg), L-glutamic acid, glycine (25 to 2500 μg), L-histidine, L-lysine, DL-methionine, L-proline, DL-serine and DL-threonine (50 to 5000 μg each) are determined with *Leuc. mesenteroides*, and DL-*iso*leucine, L-leucine, DL-phenylalanine, DL-tryptophan (25 to 2500 μg), L-tyrosine (25 to 2500 μg), L-glutamic acid and DL-valine (50 to 5000 μg each) with *Lb. arabinosus*.

IV. Examination of the determination of amino acids. Hisao Kojima and Yutaka Matsuya. *Ibid.*, 1958, **32** (2), 106–110.—Determination of L-lysine, DL-methionine (with *Leuc. mesenteroides*), L-glutamic acid and DL-phenylalanine (*Lb. arabinosus*) was carried out with various samples. The variation is <10% and no interference results from <20% of NaCl. Substances affecting the diffusion of the amino acid interfere.

V. Attempts to decrease the time for determination. Hisao Kojima and Yutaka Matsuya. *Ibid.*, 1958, **32** (3), 189–192.—The time taken for the development of the colony decreases with increasing concn. of the incubated micro-organism, but the boundary becomes less distinct with prolonged cultivation. By the use of 1% *Sacch. carlsbergensis* or *Lb. arabinosus*, 10 hours' culture suffices. The agar concn. has little effect on the result. K. SAITO

3786. **Spectrophotometric determination of pyridoxal-5-phosphate.** V. Bonavita and V. Scardi (Inst. of Human Physiol., Univ. of Naples, Italy). *Anal. Chim. Acta*, 1959, **20** (1), 47–50.—Pyridoxal-5-phosphate (**I**) is determined by measuring the change in the u.v. absorption spectrum which occurs after treatment with KCN at pH 7·4. *Procedure*—To the sample (3 ml containing <75 μg of **I**) add KCN

soln. (0·1 ml, 0·03 *M* in 0·2 *M* phosphate buffer). Heat at 50° for 45 min. and compare the extinction at 385 mμ with a similar sample containing phosphate buffer only. The difference is referred to a calibration curve. The method is specific and much less tedious than enzymic methods.

W. T. CARTER

See also Abstracts—**3667**, Determination of vitamin B_{12}. **3705**, Determination of iodine in foods. **3737**, Determination of nicotinic acid. **3802**, Determination of nicotinic acid in feeding-stuffs.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

3787. **Comparative phenolic spot tests. Application to some air particulate fractions.** G. E. Inglett and J. P. Lodge (U.S. Public Health Service, Cincinnati, Ohio). *Anal. Chem.*, 1959, **31** (2), 248–249.—Comparative spot tests in which four different reagents were used (diazotised sulphanilic acid, formaldehyde - H_2SO_4, Millon's reagent and 4-aminophenazone) were applied to 34 phenols and the characteristic colours and lower detection limits were determined. The tests were applied to the weak acid fractions of the benzene-soluble particulate matter from 11 U.S. cities. Samples from two indicated the presence of phenolic compounds. Evidence was obtained for the presence of flavonoids, presumably derived from pollen in the samples.

G. P. COOK

3788. **Determination of small quantities of ozone in room air.** G. A. Hunold and W. Pietrulla (Lab. f. chem. Toxikol., Bundesgesundheitsamt, Berlin-Dahlem). *Z. anal. Chem.*, 1959, **165** (1), 20–28.—The method of Deckert (*cf. Anal. Abstr.*, 1957, **4**, 882), in which paper impregnated with $Fe(SCN)_3$ is used, is unsuitable for the quant. determination of 0·001 to 0·2 mg of O_3 per cu. metre (0·005 to 0·1 p.p.m.). Thorp's method (*Anal. Chem.*, 1940, **12**, 209), in which buffered KI soln. is used for absorbing O_3, is adapted for this purpose. The KI soln. (2 *N*) is light-sensitive, and should be made with very pure water. The streaming velocity of the air is conveniently 1 litre per min. The determination of 0·1 p.p.m. of O_3 then takes 2·5 hr. and is accurate to within ±10%. Blanks must be run with O_3-free air.

J. P. STERN

3789. **Determination of nitrogen dioxide and nitric oxide in air.** W. E. Gill (Gen. Electric Co., Hanford Atomic Products Operation, Richland, Wash.). *U.S. Atomic Energy Comm.*, Rep. HW-30331 (Rev.), 1958, 23 pp.—Several methods of NO_2 sampling and analysis were investigated. A simple method was developed for the prep. of known concn. of NO_2 and NO. In 50-ml syringes containing NO_2-absorbing reagents of the Griess - Ilosvay type, colour development occurred rapidly for ≃1 hr. For greatest accuracy, colour development should be allowed to continue for 1 hr. before readings are taken. Griess - Ilosvay type reagents were not specific for NO_2 in that they reacted significantly with NO. The phenoldisulphonic acid method for the determination of NO_2 gave good recoveries in concn. as low as 16 p.p.m., when a 500-ml air sample was used. Approx. 40% of the NO_2, in mixtures of NO_2 and NO, was selectively adsorbed on 4 g of 12 to 20-mesh silica gel when the NO_2 concn. did not exceed 100 p.p.m.

NUCL. SCI. ABSTR.

3790. **Determination of particulate lead content in air. Results of tests in city traffic.** B. J. Tufts (Cloud Physics Lab., Dept. of Meteorol., Univ. of Chicago, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 238–241.—Airborne particles containing Pb may be detected and the size and number of particles may be determined after reaction with a satd. soln. of tetrahydroxyquinone in 50% aq. ethanol. The reagent forms a red ppt. with Pb. The air sample is drawn through a membrane filter. The membrane is then placed on a piece of blotting paper soaked in the reagent soln. Soluble lead compounds react immediately. For the detection of insol. lead compounds, the membrane is exposed to HF vapour for 1 hr., then to NH_3 fumes for 3 min., and is then brought into contact with the reagent soln. on blotting paper. After the reaction is complete the membrane is transferred to a glass slide and dried. It is then mounted with a drop of immersion oil and examined microscopically. The red spots of the lead ppt. can be counted and the lead content estimated. A definite relationship exists between the original particle size and the reaction site size. The method has been used to study the emission of Pb-containing particles from automobile exhausts. Calcium ions, Ag^+, Fe^{2+} and Fe^{3+} give no reaction, while Ba^{2+} give a greenish-yellow coloration.

F. L. SELFE

3791. **Determination of quinquevalent, tervalent and organic phosphorus in the atmosphere and in aqueous solutions.** R. May (Occupational Health Branch, Div. of Health and Safety, T.V.A., Wilson Dam, Ala., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 308–310.—The usual colorimetric methods for the determination require P to be in the orthophosphate form. Selective oxidation procedures are described for the determination of P^{III}, P^{V} and organic phosphorus when present together in aq. soln. Three aliquots of the sample soln. are treated as follows—(*i*) P^{V} is measured with no oxidising treatment; (*ii*) P^{V} is measured after oxidation of P^{III} with $(NH_4)_2S_2O_8$ in HCl soln. (0·1 *N* to 1·0 *N*); (*iii*) P^{V} is measured after oxidation of P^{III} and organic phosphorus with $(NH_4)_2S_2O_8$ in alkaline soln. (2% NaOH). In each case the measurement of P^{V} is made colorimetrically by either the molybdenum blue or the molybdovanadophosphate method. A method for atmospheric sampling is given and results are quoted.

F. L. SELFE

3792. **Determination of chlordane in air of habitations treated for insect control.** M. A. Malina, J. M. Kearny and P. B. Polen (Velsicol Chem. Corp., Chicago, Ill., U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (1), 30–33.—Chlordane is determined by drawing 1000 litres of air (5 litres per min.) through two traps each containing 30 ml of *n*-butanol. The combined butanol soln. are mixed by swirling with *n*-pentane (100 ml) and the alcohol is removed by washing with water (7 or 8 × 200 ml). The pentane is dried with anhyd. Na_2SO_4 (5 to 10 g), and evaporated to 10 ml. This soln. is then chromatographed on a Florisil column, and the chlordane is eluted with pentane (200 ml) and determined colorimetrically with alkaline methanolic diethanolamine by a modification of Davidow's method (*J. Ass. Off. Agric. Chem.*, 1950, **33**, 886). The recovery averages 80% and concn. lower than 0·005 p.p.m. can be determined.

M. D. ANDERSON

3793. **Improvements relating to the testing of water for free and combined chlorine [by means of an indicator].** A. T. Palin. Brit. Pat. 813,493; date

appl. 28.11.56.—A dialkyl derivative of *p*-phenylenediamine or a salt thereof, *e.g.*, the oxalate, sulphate or hydrochloride of dimethyl- or diethyl-*p*-phenylenediamine, is used as an indicator in conjunction with a sequestering agent, *e.g.*, sodium hexametaphosphate or EDTA or its disodium salt.

J. M. JACOBS

3794. **Rapid determination of sulphate, chloride and nitrate ion in water in a single sample.** D. Ceauşescu (Inst. for Hygiene, Timişoara, Romania). *Z. anal. Chem.*, 1959, **165** (6), 424–428.—The sample is passed through a cation-exchange resin (H form) and the eluate is analysed volumetrically. The total acid is titrated with NaOH soln., with alizarin red S (C.I. Mordant Red 3) as indicator; the H_2SO_4 is measured by titration with $Ba(ClO_4)_2$ and the HCl with $Hg(NO_3)_2$ soln. The HNO_3 content is calculated from the differences. The error is generally $<1\%$.

G. P. COOK

3795. **[Determination of] silica in water. V. Salt effect on the colorimetric determination of silica in concentrated salt solution.** Iwaji Iwasaki and Toshikazu Tarutani (Anal Chem. and Geochem. Lab., Instit. of Technol., Meguro-ku, Tokyo). *Bull. Chem. Soc. Japan*, 1959, **32** (1), 32–36 (in English).—The wavelength, the kind of salt and the concn. of salts affect the salt effect in both the molybdosilicate and molybdenum blue methods, the salt effect in the former method being greater at a longer wavelength. The effect of sulphate is greater than that of chloride. The absorbance of both the molybdosilicate and the molybdenum blue complex in a salt soln. obeys Beer's law at a given wavelength when the concn. of salt and reagents remain constant. In salt soln. containing definite amounts of silica, the absorbance decreases linearly with salt concn. under these conditions. To obtain the true silica content in concentrated salt soln. by the colorimetric method, one of the following procedures should be used. (*i*) A sample soln. is diluted with H_2O sufficiently for the salt effect to be neglected and the absorbance is then measured; (*ii*) a calibration curve is prepared with standard sodium silicate soln. containing the same concn. of salts as in the sample soln.; (*iii*) a calibration curve is prepared by means of standard sodium silicate soln. without added salts. This is used to determine the concn. of silica in the sample soln. (*A*) and in the sample soln. diluted with an equal vol. of water (*B*). The true silica content (*S*) is then given by $S = A + 2(2B - A)$.

I. JONES

3796. **Methods for measuring grease in sewage.** W. W. Ullmann and W. W. Sanderson (New York State Dept. of Health, Albany). *Sewage Ind. Wastes*, 1959, **31** (1), 8–19.—A chromatographic adsorption method developed for the differentiation in sewage between grease of petroleum and non-petroleum origin is described. Experimental data show that light petroleum and *n*-hexane are equally suitable as solvents, and that the precision and accuracy of the method are independent of the amount of oil present in the samples.

O. M. WHITTON

3797. **Determination of oil in refinery effluents by u.v. spectrophotometry.** O. Harva and A. Somersalo (Lab. of Neste Oy Refinery, Naantali, Finland). *Suomen Kem. B*, 1958, **31** (12), 384–387.—A sample of the refinery effluent is shaken with CCl_4 and diluted with CCl_4 so as to contain 10 to 100 mg per litre of waste oil. The u.v. absorption of this soln. is measured at the maximum of 260 mμ and the concn. of the oil in the sample is calculated by means of a standard oil soln. It is stated that this method gives the same precision as the usual i.r. or pycnometric methods, whereas gravimetric methods give low values.

E. SJÖSTRÖM

3798. **Behaviour and determination of radium-B, radium-D and thorium-B in natural waters.** G. Alberti, C. Bettinali and F. Salvetti (Chem. Lab., Geomineral. Div., C.N.R.N., Inst. Gen. and Inorg. Chem., Univ. of Rome). *Ann. Chim., Roma*, 1959, **49** (1), 193–198.—Radioactive lead isotopes in samples of water are extracted as the dithizonates and the rate of decay in β-activity is compared with that of standard soln. of Ra-B, Th-B and Ra-D. The half-lives of these 3 isotopes differ considerably, and hence the concn. of the individual isotopes may be determined. By the method described it is also possible to determine the contents of Rn and of the Ra and ThX ultimately produced.

A. G. COOPER

See also Abstract—**3648**, Determination of Ca in water.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

3799. **Determination of boron in treated wood.** W. J. Wilson (Forest Res. Inst., Whakarewarewa, Rotorua, N. Zealand). *Anal. Chim. Acta*, 1958, **19** (6), 516–519.—Two modified procedures are described, one for rough sorting of impregnated timber and one for more precise determinations. For rough sorting, a cross-section is sprayed with turmeric extract (10% in ethanol), allowed to dry and then sprayed with an acid soln. (20 ml of conc. HCl in 80 ml of ethanol saturated with salicylic acid). With *Pinus* species, the second soln. is modified (10 ml of HCl, 90 ml of ethanol and 10 g of salicylic acid). After drying, the wood shows distinct gradations of colour corresponding to the boric acid content (bright red ≡ 0·3%, brown - red ≡ 0·25%, yellow - brown ≡ 0·25%, yellow ≡ 0·1%). Samples showing $<0{\cdot}25\%$ are analysed chemically. For precise determinations the standard ashing technique is modified by adding to 5 g of powdered wood 10 ml of $Ba(OH)_2$ soln. (7·5% in 1% v/v HNO_3) and drying before ignition.

T. R. ANDREW

3800. **Determination of urea in agricultural nitrogen solutions.** D. K. Gullstrom and P. A. Demkovich (Res. Dept., Standard Oil Co., Whiting, Indiana). *J. Agric. Food Chem.*, 1959, **7** (1), 26–27.—Urea is determined in the presence of NH_3 and/or NH_4NO_3 by decomposing with HNO_2, absorbing the CO_2 evolved in a soln. of $Ba(OH)_2$ and $BaCl_2$, and titrating the excess of base. Dissolved CO_2 is first removed from the soln. by adding H_2SO_4 and bubbling with N, before adding $NaNO_2$. The method has proved simple and rapid in routine use, and is repeatable to $\pm 2{\cdot}0\%$ of the urea present.

M. D. ANDERSON

3801. **Colorimetric determination of phosphoric acid in fertilisers by the molybdovanadophosphate method. II. Effect of ingredients and masking.** Mitsunari Matsubara (Sumitomo Chem. Ind., Niihama, Ehime-ken). *Japan Analyst*, 1958, **7**

(9), 571–578.—The effect of various ingredients in superphosphate fertilisers was examined by the use of the reagent reported in Part I (*cf. Anal. Abstr.*, 1959, **6**, 2381). The effect of silicic acid decreases with increase in HNO_3 concn., but the colour fades faster in $HNO_3 > N$. In the absence of citric acid, the following composition appears to be the best—NH_4VO_3 1·12 g, $(NH_4)_2Mo_7O_{24}.4H_2O$ 27·0 g, and HNO_3 (sp. gr. 1·38 to 1·40) 250 ml per litre (20 ml for <8 mg of P_2O_5 per 100 ml of the final soln.). In the presence of citric acid (0·34 g), the amount of molybdate is increased to 50 g and the final concn. of HNO_3 is adjusted to 0·7 *N*. K. SAITO

3802. **Chemical method for estimation of niacin [nicotinic acid] in poultry feeds and premixes.** V. S. Mohan, B. L. Reid and J. R. Couch (Dept. of Poultry Sci. and Biochem. and Nutrition, Texas A & M System, College Station, U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (1), 42–44.—Nicotinic acid is determined in feeding-stuffs by autoclaving with 1 *N* H_2SO_4, filtering, decolorising the filtrate with permanganate if necessary, neutralising to pH 6·5 to 6·8, and treating with cyanogen bromide to produce a colour which is measured at 420 mμ. Recoveries of added nicotinic acid averaged 98·6%, and results agreed well with those by microbiological assay. M. D. ANDERSON

3803. **Chromatography of organic insecticides. I. Separation on paper treated with 2-phenoxyethanol [phenylCellosolve].** Takashi Shishido and Masana Suwanai (Nat. Inst. of Agric. Sci., Nishigahara, Kita-ku, Tokyo). *J. Agric. Chem. Soc. Japan*, 1958, **32** (12), 956–960.—By the use of a mixture of 2-phenoxyethanol and acetone (5 : 1, by vol.) as stationary phase, and a mixture of *n*-hexane, $CHCl_3$, benzene and methyl cyanide as developer, 25 organic insecticides, including various organophosphorus and chlorine compounds, were examined and the R_F values determined. For chloro compounds, *n*-hexane saturated with methyl cyanide was the best developer and for phosphorus compounds a mixture of *n*-hexane, $CHCl_3$ and benzene (*e.g.*, 10 : 2 : 1) was suitable. The separation of Isochlorthion, parathion-ethyl and O-ethyl O-*p*-nitrophenyl phenylphosphorothionate was not achieved. K. SAITO

3804. **Application of Janovsky's and Mohler's reactions to the detection of benzene hexachloride [hexachlorocyclohexane].** E. Rathenasinkam (Gov. Analyst's Lab., Colombo, Ceylon). *Analyst*, 1958, **83**, 688–689.—In the test based on Janovsky's reaction, 0·5 to 1 ml of nitration acid (5 g of KNO_3 in 100 ml of H_2SO_4) is placed in a Cavett flask (*Analyst*, 1954, **79**, 125) and 0·2 ml of a soln. of hexachlorocyclohexane (**I**) in glacial acetic acid, with three fragments of magnesium wire, is added to the stopper-cup and the stopper is immediately inserted. After 30 min. the cooled nitration acid is diluted with water (20 ml) and extracted with diethyl ether. The extract is washed with 2% NaOH soln. and saturated NaCl soln. and is filtered through cotton wool and Na_2SO_4 into a test-tube. Liquid paraffin (4 drops) is added to the filtrate, the ether is removed by evaporation, the residue is dissolved in 1 ml of a mixture of acetone and abs. ethanol (1 : 1), 0·1 ml of a 4% soln. of KOH in methanol is added and the tube is stoppered. A crimson colour develops in 2 min. The test is sensitive to 5 μg of **I**. In the test based on Mohler's reaction, the dechlorination and nitration are carried out as described above, but with only 0·5 ml of nitration acid. After 30 min. the nitration acid is diluted with 2·5 ml of water, 5 ml of 25% aq. NH_3 is added and then 2 ml of 2% hydroxyammonium chloride soln., and the mixture is transferred to a stoppered tube. A violet colour develops slowly. The test is sensitive to 0·25 mg of **I**.
A. O. JONES

See also Abstracts—**3527**, Determination of Co in agricultural material. **3648**, Determination of Ca in soil extracts. **3814**, Soil-perfusion apparatus.

5.—GENERAL TECHNIQUE AND APPARATUS

General

3805. **Precision of some procedures in pharmaceutical analysis. I. Use of a pipette and a burette.** A. R. Rogers (Sch. of Pharm., Brighton Tech. Coll., England). *J. Pharm. Pharmacol.*, 1958, **10**, Supplement, 98T–105T.—Estimates have been made of the variance associated with the calibration of a number of 10- and 20-ml pipettes and 50-ml burettes of Grade-B quality, and of the variance associated with their use by students. Comparison with the variance of the results of students performing simple titrations with this apparatus indicates that the chief components of the latter variance have been identified. A. R. ROGERS

3806. **New method for the measurement of the density of liquids.** J. Krutzsch (Villacher Strasse 52, Munich, Germany). *Chimia*, 1958, **12** (11), 324–325.—An apparatus utilising the comparison of heights of liquid columns in determining ρ is described (*cf. Klin. Wochschr.*, 1943, **22**, 469). A capillary tube dips into the test liquid and its open top communicates with a U-tube with one short limb. Both tubes are connected to a syringe acting as a piston pump. The U-tube contains a non-volatile oil of known ρ. When the syringe piston is retracted, the liquids rise in their respective tubes. The bulk of the test liquid is then lowered manually so that contact between its surface and the liquid column is broken. The test liquid is allowed to rise until the head of the column is in a horizontal part of the capillary. The apparatus is then isolated from the syringe by closing a screw-clip and the lengths of the liquid columns are measured. Viscosity and surface tension have no effect, and temperature changes have little effect on the determinations, which require 3 ml of liquid, occupy 2 min., and are accurate to three decimal places. The method is used for pharmaceutical and clinical fluids and extracts. J. P. STERN

3807. **Automatic reader for precision balances.** L. R. Macurdy and H. A. Bowman (Nat. Bur. of Standards, U.S.A.). *Instrum. and Automation*, 1958, **31** (12), 1972–1974.—A photo-electric beam-position recorder automatically indicates beam-position and turning points with a precision of 0·0001 in., giving an approx. 40-fold increase in readability sensitivity. G. SKIRROW

3808. **New absorption pipette and magnetic shaker for the constant-volume gas-analysis apparatus.** P. R. Chapman and P. A. Murche (N. Thames Gas Board, Fulham, London). *Chem. & Ind.*, 1958, (46), 1504–1505.—Diagrams of the pipette and shaker are given. The top of a plunger containing a soft iron core and weighted with mercury floats on

the mercury surface in the pipette. The plunger is caused to oscillate 100 times per min. by a make-and-break current through a 9-ohm, 12-V a.c. solenoid. A double cam fitted to a 12-V, 50 r.p.m. motor depresses a spring-loaded bar resting against the control button of a micro-switch in the solenoid circuit; the current to solenoid and motor is controlled by a timer switch. Reagents in reservoirs are connected to the pipette through a manifold and are protected by a layer of paraffin oil; furnaces are electrically heated and easy regeneration of the catalyst is possible. The complete analysis time for fuel gas is 75 min. P. D. PARR-RICHARD

3809. **Automatic apparatus for elementary organic analysis.** F. Vojtěch (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Průmysl*, 1958, **8** (12), 633–636.—Three types of automatic apparatus for organic analysis and their use are described. (*i*) A simple apparatus for the determination of N based on the Dumas - Zimmerman principle (*Mikrochemie*, 1943, **31**, 42), in which the combustion is carried out with successive switching of the heating circuits; (*ii*) apparatus for the determination of C and H according to Pregl's procedure, suitable also for rapid catalytic combustion (Synek and Večeřa, *Chem. Listy*, 1955, **49**, 1891) on the semi-micro- and micro-scale (Körbl, *Chem. Listy*, 1955, **48**, 858); (*iii*) universal apparatus for the determination of C,H,N,S and halides on the semi-micro- and micro-scale; two samples can be analysed simultaneously. Descriptions and illustrations of the apparatus together with manipulative details are given. J. ZÝKA

3810. **Mineralisation apparatus for the determination of nitrogen by the Kjeldahl and phosphorus by the Belcher and Godbert methods.** X. Bilger and G. Mangeney. *Bull. Soc. Chim. France*, 1958, (11–12), 1539–1540.—An apparatus is described in which fumes from a Pyrex-glass mineralisation tube with a side-arm are removed through a small glass manifold into a vacuum filtration flask. The tube is loosely stoppered with a flattened glass ball through which passes a Gernez tube made by forming a bulb on the end of a 4-mm tube and drawing in a concavity of 1 to 2 mm. E. J. H. BIRCH

3811. **Apparatus for the controlled flame combustion of filter-paper.** M. Homma and A. E. Greendale (Naval Radiological Defense Lab., San Francisco). *U.S. Atomic Energy Comm.*, Rep. USNRDL-TR-285, 1958, 16 pp.—A new apparatus and technique are described for the controlled flame combustion of filter-paper and cloth. The sample is burned in an atmosphere of oxygen at a reduced pressure within a Pyrex-glass cylinder. A detailed description is given of the operation of the apparatus. The many advantages of this system over previous methods are enumerated. The apparatus can be scaled up or down in size and can also be used with gases other than oxygen. Since it is possible to contain the sample completely during the combustion and to collect the products of combustion, it appears to be an extremely efficient system for quant. determinations and for use with radioactive materials and toxic chemicals.

NUCL. SCI. ABSTR.

3812 **Improvements in or relating to devices for determining the oxidising or reducing characteristics of an atmosphere.** Robertshaw-Fulton Controls Co. [Inventor: C. D. Lawhon]. Brit. Pat. 812,607; date appl. 4.5.56. U.S.A., date appl. 8.8.55.—The device comprises a pair of thermocouples one of which has a housing (*e.g.*, of copper oxide) thermally affected by a reducing atmosphere, while the other has a housing (*e.g.*, of carbon) which is thermally affected by an oxidising atmosphere. The thermocouples, which are inserted in suitable apertures in the wall of the chamber, are connected so that their e.m.f. are opposed. J. M. JACOBS

3813. **Quantitative sedimentation analysis with a sedimentation pipette.** W. Kromrey. *ChemikerZtg*, 1959, **83** (1), 13–16.—In the technique described, the normal gravimetric analytical procedures are used for the determination of ions, but the amount of pptd. material is measured as the height of a column of solid, and not by weight. It is shown that this height (in mm) is related to the amount of ion present in soln., and that by using standard soln. a direct conversion of mm to mg is possible. The pptn. is carried out in a sedimentation pipette (described) and the ppt. is centrifuged under standard conditions of speed and time. Methods are given for the determination of 20 ions, and of picric acid, and by the use of suitable pptg. agents this list can be extended. The technique is relatively simple, and each determination requires only 2 to 5 ml of soln. It can be used for the analysis of blood, serum and urine. D. B. PALMER

3814. **Modified design of the Audus soil-perfusion apparatus.** C. M. Sims and F. M. Collins (Dept. of Bacteriol., Univ. of Adelaide, S. Australia). *Analyst*, 1958, **83**, 699–701.—In the apparatus described by Lees and Quastel (*Biochem. J.*, 1946, **40**, 803), soil was continuously perfused with dil. $(NH_4)_2SO_4$ soln., the rate of nitrification of the NH_3 being followed by determination of NO_2^- in the perfusate. The modified form of this apparatus devised by Audus (*Nature*, 1946, **158**, 419), now further modified, is described. Graphs of results obtained with the modified apparatus resemble those reported by Lees and Quastel (*loc. cit.*), the only difference in the performance of the modified apparatus being the transient accumulation of nitrite-N in the perfusate before NO_2^- are detected. The apparatus is in one piece and among its other advantages are its smallness, its independence of external support, and the possibility of accommodating more than 20 units operated by a single water-pump through a manifold fitted in an incubator 4 ft. × 3 ft. × 2 ft. A. O. JONES

3815. **Improvements in or relating to viscometers.** "Shell" Research, Ltd. [Inventor: J. F. Hills]. Brit. Pat. 813,735; date appl. 2.8.57.—A bob is mounted in a fixed cup so that it is free to rotate about a spindle to which a second cup is rigidly attached and hence also rotates about the same axis. A second bob is mounted in the second cup and is coupled to an electric motor so that it rotates about a second spindle. In operation, one of the cups is filled with liquid of known viscosity and the other with the sample of which the viscosity is required. The latter is determined from the viscosity of the first liquid and the relative rates of rotation of the bobs. J. M. JACOBS

Chromatography, ion exchange, electrophoresis

3816. **General method for detection and recording of component bands in chromatography with liquid eluents.** J. C. Sternberg and L. M. Carson (Michigan State Univ., E. Lansing, U.S.A.). *J. Chromatography*, 1959, **2** (1), 53–57.—A detector for use with

paper, string or column chromatography is described. Two wicks are situated in a temp.-controlled cell filled with the satd. vapour of the eluting solvent. One wick is continuously satd. with the eluent and the other with the eluate from the column. The arrival of a dissolved component causes a change in the v.p. of the eluent and hence in the evaporative heat-loss of that wick. The temp. difference between the wicks is measured by thermistors connected to a bridge circuit and recorder. The method is of wide application.

G. BURGER

3817. **Apparatus for the quantitative introduction of liquid samples into chromatographic columns.** M. Singliar and J. Brida (Res. Inst. of Acetylene Chem., Nováky, Czechoslovakia). *Chem. Prûmysl*, 1958, **8** (11), 588–589.—The apparatus described is easily constructed. The sample is sealed into a glass ampoule, and placed in an easily destructible small holder inserted in the chromatographic column immediately before the filling. A small iron bar is moved electromagnetically to break the ampoule, the sample is evaporated and transferred into the column by the carrier gas. The apparatus is suitable for the handling of 5 to 20 mg of compounds having b.p. from −15° upwards.

J. ZÝKA

3818. **Fraction-collector modifications.** E. A. Talley (E. Reg. Res. Lab., Agric. Res. Service, U.S. Dept. of Agric., Philadelphia, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 317–318.—The two modifications described are used in the ion-exchange chromatography of amino acids. A capillary inflow arm is substituted for the wider tube frequently used with drop-counting fraction collectors; this minimises the uptake of impurities from the laboratory air and improves the uniformity of dropping of the eluate. An auxiliary counter is used to switch the control contacts of the relay of the heating bath, which controls the temp. of the columns, from one thermostat to another at any given fraction number.

A. R. ROGERS

3819. **New paper-chromatographic procedure.** H. Halbensteiner (Fed. Inst. for Testing Veg. Products, Geisenheim/Rhg, Germany). *J. Chromatography*, 1959, **2** (1), 113–114 (in German).—A procedure for horizontal chromatography is described in which the chromatogram can be extended by moving the wick and the paper.

G. BURGER

3820. **Circular paper chromatography.** A. Miss and F. Segal (Chem. Res. Inst., Min. for Petroleum and Chem. Ind., Bucharest, Romania). *Z. anal. Chem.*, 1959, **165** (1), 1–5.—The advantages of circular over ascending or descending paper chromatography are discussed, and an improved and simplified technique is described in which the paper is held horizontally between two Petri dishes and fed with solvent by means of a thread of mercerised cotton, artificial silk, wool, or other material. The thread dips into the solvent and passes through a hole at the centre of the paper where the material to be developed is placed. The rate of solvent transport can be controlled by choice of the material and length of the thread. Reproducibility is very good and the method has been satisfactorily used for the separation of amino acids, higher fatty acids, sugars, etc.

J. P. STERN

3821. **Semi-automatic multi-pipetting device for paper chromatography.** J. W. Porteous (Marischal Coll., Univ., Aberdeen, Gt. Britain). *J. Chromatography*, 1959, **2** (1), 58–64.—The apparatus described comprises a paper holder and a pipette holder. Large vol. of soln. can be applied in 2 to 5-μl portions to 12 papers simultaneously. Provision is made for drying each portion before the next addition. Constructional details are given.

G. BURGER

3822. **Simple ascending paper-strip chromatography device for rapid exploratory studies.** G. J. Miller and R. J. McColloch (Dept. of Agric. Res. Chem., Univ. of Wyoming, Laramie, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 320–321.—A glass tube (1 in. diam.) is used as the chromatography chamber and the paper strip is suspended from a thermometer-suspension stopper and held taut by a glass weight hung from the bottom of the paper strip.

A. R. ROGERS

3823. **Appearance of artefacts on chromatograms of quaternary ammonium compounds.** C. Crocker (Inst. of Biophys., Univ. of Brazil, Rio de Janeiro). *J. Chromatography*, 1959, **2** (1), 115–116.—Residual traces of trichloroacetic acid in concn. as low as 0·2% can produce artefacts in chromatograms of quaternary ammonium compounds run with alkaline solvents. They have been observed with choline and several synthetic curares. Similar artefacts have been observed by other authors in chromatograms of adrenaline, histamine and thyroxine run with acid solvents.

G. BURGER

3824. **Review of gas-liquid chromatography.** C. J. Hardy and F. H. Pollard (Univ., Bristol, England). *J. Chromatography*, 1959, **2** (1), 1–43.—The published work on the theoretical principles, apparatus, techniques and applications of gas-liquid chromatography is critically reviewed, with 619 references.

G. BURGER

3825. **New apparatus for gas-chromatographic analysis.** W. Virus (Dr. Virus KG, Bonn, Rheinweg 159). *Erdöl u. Kohle*, 1958, **11** (12), 867–868.—The "Gasofract" gas chromatograph is described. A 16-metre column, built from sections, is housed, together with the thermal-conductivity cell, preheater and inlet system, in a thermostat capable of maintaining the temp. constant to ±0·1°. The working range is 40° to 250°. All the column controls and the bridge circuit are contained in the column unit. The sample may be liquid or gaseous. A separate recording unit records and integrates the chromatogram, so that peak areas are shown directly. Seven sensitivity ranges are available on a chart width of 25 cm. Suitable stationary phases are recommended for several separations.

G. BURGER

3826. **Analysis of gases.** Esso Research and Engineering Co. Brit. Pat. 811,744, date appl. 1.8.56. U.S.A., date appl. 1.8.55. (Addition to Brit. Pat. 762,008, dated 2.2.54.)—The method of analysis claimed in Brit. Pat. 762,008 is improved by separating the gaseous mixture into various fractions by means of chromatography and using the fractions from the chromatographic separation as the first mixture of gases in the method described in Brit. Pat. 762,008.

J. M. JACOBS

3827. **Improvements in and relating to gas analysing apparatus.** Cambridge Instrument Co., Ltd. [Inventors: G. Jessop and H. V. Beck]. Brit. Pat. 812,714, date appl. 25.6.56.—In apparatus embodying a katharometer or other means involving the utilisation of temp. changes of electrically heated

thermal elements, these elements are supplied from a mains unit comprising a transformer having a low leakage inductance (*e.g.*, 100 μH) and a secondary winding having, or connected in series with, a resistance of ≮1 ohm. J. M. JACOBS

3828. **Process for the continuous separation of gas mixtures by means of gas chromatography.** Deutsche Erdol-A.-G. Brit. Pat. 810,767, date appl. 13.11.57. Germany, date appl. 17.11.56.—The gas mixture to be separated, which comprises slow- and fast-moving components or groups of components and a carrier gas, is passed continuously through a separation column containing a solid phase moving in countercurrent to the direction of flow of the gas mixture, and at a velocity intermediate between the velocity of the slowest- and that of the fastest-moving components. J. M. JACOBS

3829. **Continuous gas chromatography. Procedure for continuous two-phase countercurrent separation of a multicomponent mixture applying temperature gradients.** W. Kuhn, A. Narten and M. Thurkauf (Phys.-Chem. Inst., Univ., Basel). *Helv. Chim. Acta*, 1958, **41** (7), 2135–2148.—Separation of several components may be effected by running two mobile phases in countercurrent and maintaining a temp. gradient along the column. As the distribution coeff. vary with temp., various components collect at different places along the column and may be removed.

M. H. SAWISTOWSKA

3830. **Characterisation of organic compounds by gas chromatography. I. Retention indices of aliphatic halogen compounds, alcohols, aldehydes and ketones.** E. Kováts (Org.-chem. Lab., Tech. Hochschule, Zürich). *Helv. Chim. Acta*, 1958, **41** (7), 1915–1932.—The retention index, a value related to the vol. of the gas constituting the stationary phase at the maximum concn. of the chromatographed substance, is characteristic for different substances and provides means of identification. Data for a number of compounds are tabulated. For the separation of two compounds there must exist a certain minimum difference in the values of their retention indices.

M. H. SAWISTOWSKA

3831. **Gas chromatography of polar compounds using a non-polar liquid phase.** E. C. Ormerod and R. P. W. Scott (Benzole Producers Ltd., Watford, Herts., England). *J. Chromatography*, 1959, **2** (1), 65–68.—Poor separation in the gas chromatography of polar materials with a non-polar stationary phase is due to adsorption on the support. Separation is greatly improved by coating brick dust with an equal weight of silver by the Rochelle salt method. The ground brick is degreased, treated with the silvering soln. and de-gassed under reduced pressure before the reducing soln. is added. Deposition of gold on brick was patchy and unsatisfactory. Coatings of gold on silvered brick or of nickel from $Ni(CO)_4$ are suggested as possible improvements.

G. BURGER

3832. **Micro-sample introduction system for gas chromatography.** R. L. Bowman and A. Karmen (Nat. Heart Inst., Bethesda, Md., U.S.A.). *Nature*, 1958, **182**, 1233–1234.—The apparatus described enables small vol. of samples in the microgram range to be directly introduced into the system. Samples are sealed in small glass capillaries in which the vol. can be accurately measured; the capillary is crushed in the gas stream at the column inlet. H. F. W. KIRKPATRICK

3833. **Collection unit for gas - liquid chromatography under reduced pressure.** B. M. Craig, T. M. Mallard and L. L. Hoffman (Prairie Reg. Lab., Nat. Res. Council, Saskatoon, Saskatchewan, Canada). *Anal. Chem.*, 1959, **31** (2), 319–320.—In the unit described, each component emerging from a gas-chromatographic column can be collected separately without disturbing the pressure in the system. The unit is also suitable for operation at atmospheric pressure. K. A. PROCTOR

3834. **Response time and flow sensitivity of detectors for gas chromatography.** L. J. Schmauch [Res. Dept., Standard Oil Co. (Indiana), Whiting, Ind., U.S.A.]. *Anal. Chem.*, 1959, **31** (2), 225–230.—A quantitative relationship exists between band shape and the ratio of response time to band width in gas chromatography. To prevent band broadening and asymmetry, the response time of the detector must be small. K. A. PROCTOR

3835. **Apparatus for automatic colouring and decolorisation of electrophoresis papers.** O. P. Foss and B. Andersen (Central Lab., Ullevål Hosp., Oslo, Norway). *Scand. J. Clin. Lab. Invest.*, 1958, **10** (3), 344.—The papers are carried on a plastic framework which is rotated in a semi-cylindrical ceramic trough by an electric motor. A plastic hood covers the trough and frame. The trough contains the staining or decolorising soln., into which the papers dip. Rotation times depend on the staining technique employed; with a satd. soln. of Amido-black 10B (C.I. Acid Black 1) in methanol, a rotation time of 20 min. is usually sufficient.

D. W. MOSS

Optical

3836. **Transmission characteristics of some interference filters for use in flame photometers.** R. D. Bond and H. C. T. Stace (C.S.I.R.O., Div. of Soils, Adelaide, S. Australia). *Analyst*, 1958, **83**, 679–683.—The transmission characteristics of seven combination interference-absorption filters and one gelatin absorption filter for the isolation of the sodium D line have been determined. The transmission characteristics were determined spectrophotometrically and the filters were then examined in a flame photometer to measure the interference caused by radiations emitted by other elements during the determination of Na in soil extracts and minerals. To determine the magnitude of these expected interferences, soln. containing 20 milli-equiv. per litre of salts of Li, K, Rb, Cs and Ca were examined in the flame photometer and their apparent Na content determined with each filter. One filter indicated no apparent Na content after correction for Na present as impurity except with the soln. of $CaCl_2$. With the other filters the apparent Na found (corrected) ranged from 0·003 to 0·132 milli-equiv. per litre. The component errors contributing to the total error are discussed.

A. O. JONES

3837. **High-sensitivity, recording, scanning flame spectrophotometer.** M. T. Kelley, D. J. Fisher and H. C. Jones (Nat. Lab., Union Carbide Nuclear Co., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 178–183.—The instrument described possesses

the advantages of increased precision and dependability (arising from the use of a chart recorder), reduction of hazards in radioactive analyses, and the reduction of flame, background, anion and salt interferences. Generally, the relative standard deviation for analyses is $<1\%$ and linear calibration curves are obtained over reasonable concn. ranges. Considerations governing the choice of various components such as the recorder, monochromator and photomultipliers are discussed.
K. A. PROCTOR

3838. **Three new spectrophotometers.** E. Lüscher (Metrohm A.-G., Herisau, Switzerland). *Appl. Spectroscopy*, 1958, **12** (6), 172–174.—Three commercial instruments are described—an interference filter colorimeter (400 to 700 mμ), a prism spectrophotometer (300 to 750 mμ) and a silica prism - glass prism - grating spectrophotometer (210 mμ to 5 μ).
K. A. PROCTOR

3839. **Local spectral analysis.** A. G. Komarovskiĭ. *Tsent. Nauch.-Issled. Tekhnol. i Mashin.*, 1957, **84**, 184–198.—A universal generator, producing, in addition to the usual spark and arc discharges, a high-frequency discharge, a strong spark pulse discharge of low voltage, and an a.c. arc pulse discharge, is described and the procedure outlined. A copper wire, 8 to 9 mm in diam., shaped to a truncated cone with a working surface of 1 to 1·5 sq. mm, was found more satisfactory as an upper electrode than aluminium, nickel, iron or carbon. The high-frequency discharge was suitable for the spectral analysis of surface layers along the edges of hot-cracks in welds of high-alloyed steel. The surfaces of these cracks were of a different composition than the metal of the weld and had to be removed by grinding. The most suitable spectral line-pairs for the determination of Mo, Ni, Si, Mn, Cr, W, Ti, V, Co, Al and Nb were determined and tabulated. The low-voltage spark pulse discharge, lasting 10^{-3} to 10^{-4} sec., one impulse of which was satisfactory for an analysis, gave additional lines which were absent in other light sources; the lines of air were also absent so that it could be used for the determination of H, N and O in steel. To localise the surface of analysis, prevent flame migration, and intensify the lines, the spark contact was made through a hole 0·1, 0·5, 1·0 or 1·2 mm punctured through a layer of insulating plastic or shellac 1 or 0·2 to 0·6 mm thick. CHEM. ABSTR.

3840. **Constant-current arc source for spectrochemical analysis.** L. E. Owen (Tech. Div., Goodyear Atomic Corp., Portsmouth, Ohio, U.S.A.). *Appl. Spectroscopy*, 1958, **12** (6), 178.—The source described operates from a single-phase power supply, provides various controlled current outputs at different levels, incorporates ignitor and timing circuits and provides for optional earthing of the negative or positive line.
K. A. PROCTOR

3841. **Effect of spectrum carbons on spectrographic analysis.** H. H. Rüssmann (Ringsdorff-Werke G.m.b.H., Bad Godesberg-Mehlem, DBR). *Acta Chim. Acad. Sci. Hung.*, 1959, **18** (1–4), 101–119 (in German).—The basic differences between graphite and carbon electrodes are described, and the effect of both types on spectrographic analysis is discussed. The temp. of the d.c. arc with both electrodes has been found from the intensity curve of the CN bands, the carbon arc being the hotter by approx. 700° K. The phenomenon of "creeping," experienced with d.c. arcs when elements of low ionisation potential are excited, is discussed, and methods for overcoming this are suggested. The influence of the two types of electrode on the analysis of soln. has been studied, together with the effect of porosity of the electrode.
H. M.

3842. **Simple device for the spectrochemical analysis of minerals in an inert atmosphere using the Stallwood jet.** D. M. Shaw, O. Wickremasinghe and C. Yip (McMaster Univ., Hamilton, Ontario, Canada). *Spectrochim. Acta*, 1958, **13** (3), 197–201.—Details are given of a partially closed chamber, made from Pyrex-glass tube, a piece 0·75 in. in diam. and 3 in. long being attached to a piece of 0·25 in. diam. by a T-joint; with this chamber, air can be completely excluded from the arc, and cyanogen bands eliminated from the spectra. By using a gas mixture of argon and oxygen (1 : 1), overall background is reduced and sensitivity is enhanced. Preliminary work on the determination of Pb, Ga, Cu, Sn and Li in silicate minerals is discussed.
E. G. CUMMINS

3843. **Quantitative determination of solids by infra-red spectroscopy and the potassium bromide disc technique.** J. B. Jensen (Specialitetskontrollen, Copenhagen, Denmark). *Dansk Tidsskr. Farm.*, 1958, **33** (11–12), 205–220, 221–235.—The literature is reviewed and discussed. To obtain the maximum base-line extinction and satisfactory spectra, repeated grinding (usually 3 to 5 times for 1 min.) and pressing is less laborious than one grinding for the requisite time (1 hr.), and gives satisfactory results for 16 test substances. A single vibrator-grinding for 3 to 5 min. achieves the same result for 9 of the substances, but fails to do so for the others; in such cases satisfactory spectra can generally be obtained by heating the discs at 100° for 5 min. With prednisolone, which fails to give satisfactory spectra with either of the grinding techniques, the heat treatment has proved successful. (35 references.)
P. S. ARUP

3844. **Potassium bromide pellet technique.** A. L. Olsen (Chem. Div., U.S. Naval Ordnance Test Station, China Lake, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 321–322.—A simple, evacuable and easily manipulated die, designed for use in the ARL-Dietert briquetting press and employing a new technique of pressing the ½-in.-diameter pellet directly into a 1-in.-diameter ring, is described. The pressed disc fits directly into the Perkin-Elmer demountable cell holder or into the specimen holder of the high-temp. cell. The discs obtained show max. transmittances of 89·5% with a spread of 2 to 3% between max. and min. transmittances.
K. A. PROCTOR

See also Abstract—**3367**, Spectrographic techniques.

Thermal

3845. **Differential thermal analysis apparatus.** F. W. Wilburn (Pilkington Bros. Ltd., St. Helens, Lancs., England). *J. Sci. Instrum.*, 1958, **35** (11), 403–407.—The rate of heating is servo-controlled to any selected value within the range 6° to 20° per min. Curves are obtained on a chart recorder in which the pen position is determined by the potential

difference between the sample and reference materials, and the chart position is determined by the potential of the thermocouple in the reference material. Temperature differences can be detected to within 0·1°. G. SKIRROW

3846. **Automatic micro-analytical apparatus for the determination of gases in metals.** Saburo Yanagisawa, Michiharu Seki, Yoshikazu Watanabe and Shigeru Nakamura (Dept. of Appl. Chem., Fac. of Engng, Keio Univ., Tokyo, Japan). *Mikrochim. Acta*, 1959, (1), 1–8 (in English).—An apparatus is described for the automatic micro-analysis of the gases (CO_2, CO, H, N) evolved on vacuum fusion of steel (0·3 g). The passage of gas through the system is controlled by 13 electromagnetically operated mercury cut-offs which are programmed by micro-switches arranged on a rotating drum. The gases are collected in a const. vol. and the pressure after each treatment is recorded by means of a rotary McLeod gauge modified by the inclusion of a platinum resistance wire in its capillary, to permit electrical indication of pressure. The time required for evolution of gases from the sample is 10 min. and, for their subsequent analysis, 13 min. Results are quoted for a specimen containing 0·0043% of O and 0·0043% of N. T. R. ANDREW

Electrical

3847. **A polarograph with a new recording device.** J. Peizker (Polarographic Inst., Acad. Sci., Prague). *Chem. Listy*, 1958, **52** (11), 2195–2197.—The automatic compensator previously described (*Chem. Listy*, 1958, **52**, 2169) has been found suitable for the construction of a new type of pen-recording polarograph, which enables a very small reference electrode of high resistance to be used. The current between the reference electrode and the corresponding part of the polarographic circuit is completely compensated. The arrangement can be used for special cases of coulometric micro-determinations or as a potentiostatic method for use with the dropping mercury electrode when studying the products of electrode reactions under polarographic conditions. J. ZÝKA

3848. **Heyrovský circuit for derivative polarography.** Yasushi Mashiko, Noboru Hosoya and Minoru Akimoto (Hot Spring Res. Centre, Kashiwagi, Shinjuku-ku, Tokyo). *Japan Analyst*, 1958, **7** (11), 702–706.—The Heyrovský circuit for derivative polarography (*Chem. Listy*, 1946, **40**, 222) was modified so as to superpose the $\triangle$E on the mercury anode side. By this method no pulse current due to the mercury drop appears on the derivative current *vs.* applied voltage curve, provided that the dropping mercury cathode is properly adjusted. When the effect of voltage-drop due to the *iR* term is corrected, the peak voltage of the graph coincides with the half-wave potential of a reversible system (*e.g.*, Cd^{2+} in KCl) associated with a large capacitance (*e.g.* 2000 μF). K. SAITO

3849. **Influence of poly(vinylpyrrolidone) on the maxima of some polarographic curves.** L. Vignoli and B. Cristau (Lab. de Pharm. et Toxicol., Fac. de Méd. et Pharm., Marseille, France). *Chim. Anal.*, 1958, **40** (12), 458–459.—Poly(vinylpyrrolidone) (**I**) is a white powder, very soluble in water, and of mol. wt. between 30,000 and 100,000. It gives no waves in cathodic polarography. In a 0·005 *N* soln. of KCl satd. with air, a concn. of **I** of 20 mg per litre completely suppresses the oxygen maximum, and the height of the wave is not affected by 50 mg per litre of **I**. With 0·005 *M* Pb in 0·1 *M* KCl, the maxima of Pb are little affected by concn. of **I** from 1 to 5 mg per litre, but the height of the wave is affected by concn. $\geqslant$ 1 mg per litre. In a soln. of As (50 μg per ml in 2 *N* HCl), two waves are traced, the first without, the second with, maxima. The amounts of **I** (>100 mg per litre) required to efface the maxima of the second wave very seriously weaken the first wave. R. E. ESSERY

3850. **Drop-scale chronopotentiometry.** R. T. Iwamoto, R. N. Adams and H. Lott (Dept. of Chem., Univ. of Kansas, Lawrence, U.S.A.). *Anal. Chim. Acta*, 1959, **20** (1), 84–88.—Apparatus for chronopotentiometry is described in which both mercury and platinum working electrodes are used. The method is illustrated by the analysis of single drops of soln. containing I^-, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$ and Zn^{2+}. The analysis time is 1 to 2 min. and a detectable signal can be obtained from a drop containing $3·5 \times 10^{-10}$ equiv. of I^-. W. T. CARTER

3851. **Mercury chloride film anode. I. Study of the characteristics of a mercury chloride film anode by chronopotentiometric methods.** T. Kuwana and R. N. Adams (Dept. of Chem., Univ. of Kansas, Lawrence, U.S.A.). *Anal. Chim. Acta*, 1959, **20** (1), 51–60.—In Cl^- concn. of 0·2 to 0·3 *M* and using c.d. of 100 to 400 micro-amp. per sq. cm, the mercury chloride film anode can be used for the oxidation of several organic compounds. Examples are given of the determination of quinol, aniline, *p*-phenylenediamine and *p*-aminodimethylaniline by the chronopotentiometric technique. After use, the electrode can be rapidly and reproducibly cleaned by cathodic stripping. It cannot be used in soln. more alkaline than pH 5 nor in the presence of large concn. of anions which form very stable complexes with Hg^+, *e.g.*, oxalate, SO_4^{2-}, PO_4^{3-} and I^-.

II. Investigation of the characteristics of the mercury chloride film anode by voltage scan method. T. Kuwana and R. N. Adams. *Ibid.*, 1959, **20** (1), 60–67.—By using the voltage scan method, the mercury chloride film can be formed before the analysis is carried out. The electrode can then be used in the presence of substances which form very stable salts with Hg^+ or are strongly adsorbed on the mercury surface. In addition a tenfold increase in sensitivity is achieved over the chronopotentiometric method. For many organic molecules the film shows characteristics comparable to the platinum electrode and many of the $E_{\frac{1}{2}}$ (half-peak potential) values obtained are in good agreement with the $E_{\frac{1}{2}}$ values for Pt under the same conditions of pH. W. T. CARTER

3852. **Use of a glass electrode for measuring sodium in biological systems.** S. M. Friedman, J. D. Jamieson and C. L. Friedman (Dept. Anat., Univ. Brit. Columbia, Vancouver, Canada). *Proc. Soc. Exp. Biol. Med.*, 1958, **99** (3), 727–730.—The sodium electrode introduced by Eisermann, Rudin and Casby (*Science*, 1957, **126**, 831) has been developed for biological use and is found particularly useful for recording small changes in sodium concn. both in static and flowing systems. B. P. BLOCK

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	A
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic.	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_g
relative humidity	r.h
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-} PO_4^{3-}, etc., for anions.

Volume 6. No. 9, Abstracts 3367–3852 September, 1959

ANALYTICAL ABSTRACTS

A PUBLICATION OF
THE SOCIETY FOR ANALYTICAL CHEMISTRY

EDITORIAL COMMITTEE

Chairman: B. A. Ellis

Members: B. S. Cooper, C. H. R. Gentry, C. A. Johnson, H. F. W. Kirkpatrick, B. J. Walby, W. A. Waygood, K. A. Williams
and
President of the Society: R. C. Chirnside

Hon. Secretary of the Society R. E. Stuckey

Hon. Treasurer of the Society A. J. Amos

Editor: Norman Evers, B.Sc., Ph.D., F.R.I.C.

Assistant Editor: Mrs. H. I. Fisk, B.Sc.

CONTENTS

Printed and published for the Society for Analytical Chemistry by W. Heffer & Sons Ltd., Cambridge, England.
Communications to be addressed to the Editor, Norman Evers, 14, Belgrave Square, London, S.W.1.
Enquiries about advertisements should be addressed to Walter Judd Ltd., 47 Gresham Street, London, E.C.2.
Entered as Second Class at New York, U.S.A., Post Office